

I: ON THE PROPAGATION OF LARGE
DISTURBANCES IN A GAS

II: ON THE COMBUSTION OF OIL

DISSERTATIONS

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS
HOPKINS UNIVERSITY IN CONFORMITY WITH THE
REQUIREMENTS FOR THE DECREE OF
DOCTOR OF PHILOSOPHY

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THEODORE THEODORSEN

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INTRODUCTION

The general classical theory of sound is concerned with waves of infinitely small amplitudes. It was early discovered that waves of a finite amplitude behave in a radically different manner. They are not of a permanent nature but undergo a continuous change of form. The front of the waves becomes steeper and steeper until finally an apparent surface of discontinuity is created. What actually happens to the gas through this surface of discontinuity is of considerable interest. We will in the following be greatly concerned with this question. We shall derive a general relation expressing the thickness of this "surface" and subsequently draw the attention to the effect of the deviations from the conditions imposed through the differential equations, representing the wave front. We shall incidentally attempt to shed some light on the question of the extreme violence of the chemical reactions occurring in this restricted region of a "detonating" gas.

We shall in the following lines as a matter of reference indicate some of the general properties of waves or disturbances in a gas:

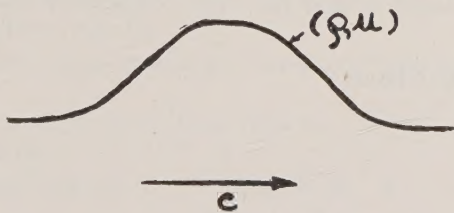


FIG. 1

Suppose we have any wave form Fig 1 advancing in the positive x-direction. Let ρ denote the density and u the velocity of the disturbed particle. We write an equation of continuity:

$$\frac{\delta \rho}{\delta t} + \frac{\delta(\rho u)}{\delta x} = 0$$

If we let the reference point move with the wave at a constant velocity $= c$, we may write correspondingly:

$$\frac{D\rho}{\delta t} + \frac{\delta}{\delta x} [\rho(u-c)] = 0 \quad . \quad . \quad . \quad . \quad I$$

In particular, if the wave is permanent and we let c be equal to the uniquely defined wave velocity, we get on putting

$$\frac{D\rho}{\delta t} = 0$$

$$\rho (c-u) = \text{constant}$$

This is a necessary condition for the permanency of the wave form. Let us apply this result to a perfect gas, assuming "a priori" that isentropic changes are possible. We superimpose on the wave an actual velocity c of the gas as a whole against the direction of propagation. Since the wave is permanent it will now appear stationary in space, while the medium as a whole has a velocity c from the right to the left. The absolute velocity of any particular particle will now be equal to $c - u$.

Each particle is represented in the temperature entropy diagram by a point on a given entropy line at a temperature T corresponding to u . T_a is the temperature produced if the medium as a whole was brought to rest by an adiabatic compression. We have then with T_a as a constant and $(c - u)$ as the absolute velocity, the following equation of energy:

$$(c-u)^2 = 2gc_v (T_a - T) = 2gc_v T_a \left(1 - \frac{T}{T_a}\right)$$

and the adiabatic relation;

$$\rho = \rho_a \left(\frac{T}{T_a}\right)^{\frac{1}{k-1}}$$

Introduced in equation I, this gives:

$$\frac{D\rho}{\delta t} = - \frac{\delta}{\delta x} \left\{ \rho_a \left(\frac{T}{T_a}\right)^{\frac{1}{k-1}} \sqrt{2gc_v T_a \left(1 - \frac{T}{T_a}\right)} \right\} \text{ or with } \frac{T}{T_a} = \theta$$

$$\frac{D\rho}{\delta t} = - \rho_a \sqrt{2gc_v T_a} \frac{\delta}{\delta x} \left\{ \theta^{\frac{1}{k-1}} (1-\theta)^{\frac{1}{2}} \right\}$$

We obtain the permanent waves when the expression in the bracket is stationary with respect to x . Let θ' denote differentiation with respect to x :

$$\frac{D\rho}{\delta t} = -\rho_a \sqrt{2gc_p T_a} \theta (1-\theta) \frac{\frac{2-k}{k-1} - \frac{1}{2}}{2(k-1)} \frac{1}{(2-\theta(k+1))\theta'}$$

This shows that $\frac{D\rho}{\delta t} = 0$ only if $\theta = 1$, ($\theta = 0$) or in the more important case:

$$\theta = \frac{2}{k+1}$$

The corresponding velocity is:

$$\sqrt{2gc_p T_a} \left(1 - \frac{2}{k+1}\right)^{1/2} = \sqrt{gkRT} = c_0$$

or the velocity of sound in the medium.

To satisfy the requirement $\vartheta = \frac{2}{k+1}$ we must keep the waves

infinitely small. The expression in the above bracket is then, and only then, stationary.

In such a case the magnitude u , representing the velocity of the disturbed particle, also is infinitely small and we may put $c - u$ equal to c_0 where c_0 is the wave velocity.

The production of *large* permanent waves in a "perfect" gas is only possible if:

$(c - u)^2 \rho^2 = \text{const.}$, which is equivalent to:

$H_a - H = \text{const. } v^2$

where H is the total heat and

$$v = \frac{1}{\rho}$$

The adiabatic lines are in this imaginary case straight lines in the $p - v$ diagram.

The volume must in this case be proportional to the created velocities within a range equal to or greater than the amplitude of the waves.

I. THE HUGONIOT RELATION

R. Becker* has given a very extensive review of the existing material on propagation of large disturbances. The pioneer work in this field was done by Hugoniot** and Berthelot***. The most peculiar property at large waves is, as mentioned, that the front of the wave is tending to increase the steepness, creating what might be called a surface of discontinuity. Hugoniot's important contribution was to show that there exists a certain relation between the magnitudes describing the state of the gas *before* and *after* this surface of discontinuity. We will proceed to develop this relation in a somewhat different form.

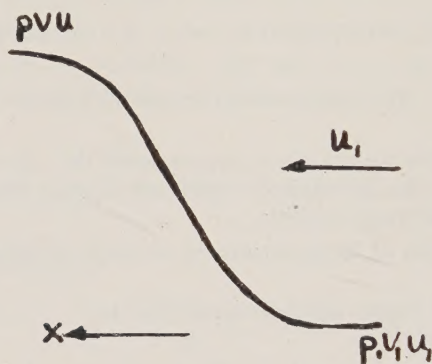


FIG. 2

* Zeitschrift für Physik 8, 1822; p. 321.

** Journal de l'école polytechnique, Paris, Vol. 57, 1887 and 58, 1889.

*** Sur la force des matières explosives, Paris, 1883.

Suppose the wave front in Fig. 2 has reached a stationary state and is propagated through the medium at a velocity u_1 . We impose on the medium as a whole, for the sake of simplicity in discussion, the opposite and equal velocity u_1 . In other words, instead of considering a disturbance which is propagated through a stationary medium, we will in accordance with adopted customs, assume that the medium in Fig 2 is flowing at a constant velocity u_1 from right to left. The wave front will now appear stationary in space. We consider only a plane wave in a perfect gas. Let index 1 refer to the parameters of state ahead of the wave and letters without index to those after the wave front.

We have then:

As equation of continuity:

$$m = \frac{u_1}{v_1 g} = \frac{u}{v g} \quad . \quad . \quad . \quad A$$

As equation of mementum $p_1 - p = m(u - u_1)$, or on introducing A_1

$$p_1 - p = \frac{u_1^2}{v_1 q} \left(\frac{v}{v_1} - 1 \right) \quad . \quad . \quad \text{B}$$

As equation of energy:

$$c_p (T_1 - T) = \frac{u^2 - u_1^2}{2g}$$

or also

$$\frac{c_p}{R} (p_1 v_1 - p v) = \frac{u_1^2}{2g} \left(\frac{v}{v_1} - 1 \right) \left(\frac{v}{v_1} + 1 \right) \quad . \quad C$$

Elimination of u_1 between B and C gives:

$$\frac{c_p}{R} (p_1 v_1 - p v) = \frac{1}{2} (p_1 - p) (v_1 + v) \quad \text{or}$$

$$\frac{2c_p}{p_1 v_1 R} (p_1 v_1 - p v) = \left(1 - \frac{p}{p_1}\right) \left(\frac{v}{v_1} + 1\right)$$

On putting $\frac{p}{p_1} = \pi_0$, $\frac{v}{v_1} = \omega_0$ and $\frac{2c_p}{R} = \chi$

$$\chi (1 - \pi_0 \omega_0) = (1 - \pi_0) (1 + \omega_0)$$

This equation may be rewritten on the interesting form:

$$\left(\pi_0 + \frac{1}{\chi - 1}\right) \left(\omega_0 - \frac{1}{\chi - 1}\right) = 1 - \left(\frac{1}{\chi - 1}\right)^2$$

$$\text{or with } \frac{c_p}{c_v} = k$$

$$\left(\pi_0 + \frac{k - 1}{k + 1}\right) \left(\omega_0 - \frac{k - 1}{k + 1}\right) = \frac{4k}{(k + 1)^2} \quad \text{II}$$

This relation represents the so-called Hugoniot curve in a very convenient form. We have, however, put down the preceding development mainly as a basis for discussion of what takes place in this peculiar kind of compression.

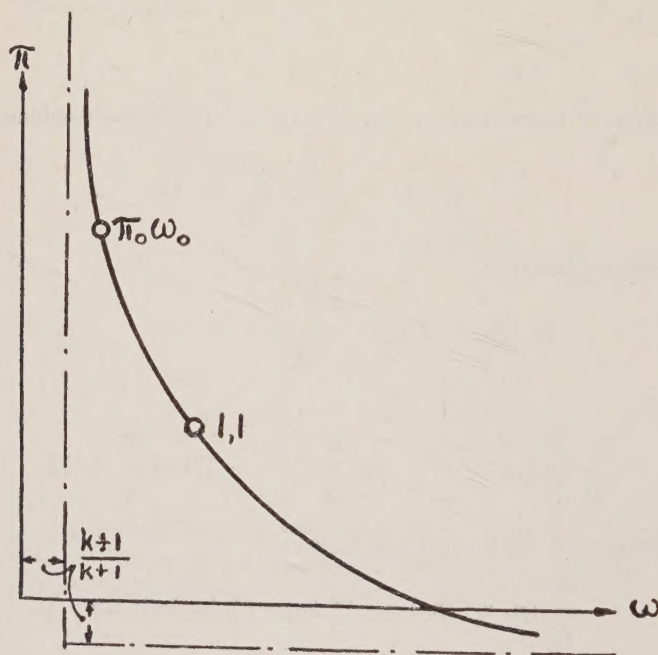


FIG. 3

Fig. 3 shows the locus of the Hugoniot points. It must be noticed that equation II, for a given value of u_1 , that is for a given disturbance, only gives *one* statepoint in the $\pi\omega$ plane. π_0 and ω_0 are uniquely determined if u_1 is given. But nothing is said about the *path of change* connecting the end point with the initial point. The investigation of this matter is of extreme importance since it ought to supply some

light on the mechanism of the extremely rapid chemical reactions taking place when combustible mixtures are detonated.

Let us give our attention to a point located arbitrarily on the wave front. Speaking in the language of Thermodynamics we will now also have to deal with the question of friction and heat conduction. R. Becker* is apparently the only one who has attacked this problem.

We want to give his interesting article published in Zeitschrift fur Physik 8, 1922 as a general reference as to the historical developments and to the existing literature. Another very complete review of this field is given in Handbuch der Physik Bd. VIII, Art. IV, and Bd. VII, Art. V.

Becker is not able to solve in general the differential equations representing the properties of the wave front. He succeeds in obtaining a relation for the thickness of the wave front in three particular cases by a method of trial (see this article). We will in the following give a general expression for the magnitude in question. We define as *thickness* of the wave front the magnitude l in figure 4.

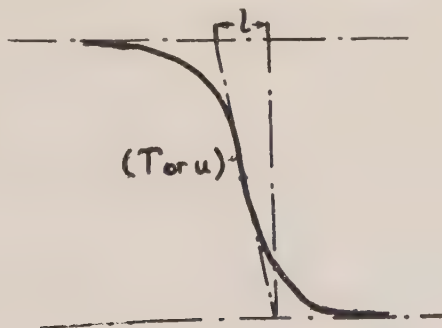


FIG. 4

II. DERIVATION OF AN EXACT EXPRESSION FOR THE THICKNESS OF THE WAVE FRONT.

We will put the heat conduction and the friction loss through the

wave front proportional to $\frac{dT}{dx}$ and $\frac{du}{dx}$ respectively. The permissibility

of this assumption will be discussed later. The equations of energy and momentum are then, respectively:

$$c_p T + \frac{u^2}{2g} - \frac{\lambda}{\gamma_1 u_1} \frac{dT}{dx} = c_p T_1 + \frac{u_1^2}{2g} \quad \text{III}$$

*R. Becker: Zeitschrift fur Physik 9, 1922, p. 339.

$$\text{and } \frac{\gamma u^2}{g} + p - \mu \frac{du}{dx} = \frac{\gamma_1 u_1^2}{g} + p_1 \quad \text{IV}$$

λ is the coefficient of heat conduction and $\mu = \frac{4}{3} \eta^*$ where

η is the coefficient of friction of the gas.

Multiplying IV by v and substituting $pv = RT$ gives

$$\frac{u^2}{g} + RT - \frac{\mu}{\gamma_1 u_1} u \frac{du}{dx} = \left(\frac{\gamma_1 u_1}{g} + p_1 \right) \frac{u}{\gamma_1 u_1} \quad \text{V}$$

We have here two equations, each containing only two unknown magnitudes T and u (or v) and the solution will give both as a function of x .

The equations do not easily yield to a direct solution due to their complicated form.

It is interesting to note that we are able to deduce a definite statement regarding the thickness of the wave front from the two equations III and IV separately.

Since in equation III: $u_1 > u$ we have:

$$\frac{\lambda}{\gamma c_p u} \frac{dT}{dx} < T - T_1 \quad \text{Consequently also:}$$

$$\frac{\lambda}{\gamma c_p u} \frac{dT}{dx} < T_2 - T_1$$

where T_2 is the final temperature.

We define a magnitude l = thickness of wave front in accordance with Prandtl and Becker:

$$l = T_2 - T_1 : \left(\frac{dT}{dx_{\max}} \right)$$

and on introduction in the inequality above:

$$\frac{\lambda}{\gamma c_p u} \frac{dT}{dx} < l \left(\frac{dT}{dx_{\max}} \right)$$

This relation is true for all values of $\frac{dT}{dx}$

So we have as final result: $l > \frac{\lambda}{\gamma c_p u}$

For comparatively small waves in air under approximately normal conditions we obtain with

*Lamb: Hydrodynamics.

$$\lambda = 0.56 \cdot 10^{-4} \frac{\text{gr cal}}{\text{cm sec } ^\circ\text{C}} \quad \gamma = 1.3 \frac{\text{gr.}}{\text{cm}^3}$$

$$c_p = 0.24 \frac{\text{gr cal}}{\text{gr. } ^\circ\text{C}} \text{ and } u = 3.3 \cdot 10^4 \frac{\text{cm}}{\text{sec}}$$

$$l > 54 \cdot 10^{-7} \text{ cm.}$$

Equation IV gives in corresponding manner the following inequality:

$$l > \frac{4}{3} \frac{\eta g}{\gamma u}$$

where l is defined by the pressure gradient.

With above data and

$$\eta = 1.69 \cdot 10^{-6} \frac{\text{kg sec}}{\text{cm}^2}$$

$$l > 51 \cdot 10^{-7} \text{ cm}$$

The two results not only are of the same order of magnitude but even approximately equal.

This could be expected:

The magnitudes η and λ are connected through the following relation:

$$\lambda = \eta g c_v \times \text{constant.}$$

This constant is dimensionless and depends on the nature of the gas. Its actual value is in our case 1.94. Replacing ηg in our second equal-

ity by $\frac{\lambda}{1.94 c_v}$ we obtain:

$$l > \frac{4}{3} \frac{k \lambda}{1.94 \gamma c_p u} \text{ or on collecting the constants: } l > 0.965 \frac{\lambda}{\gamma c_p u}$$

which expression is almost identical with our first inequality.

From the kinetic theory of gases we also have the relation

$$\lambda = \frac{1}{3} N m c L c_v = \frac{1}{3} \gamma c L c_v$$

where L is the mean free path and c is the average velocity of the molecules. See Loeb: Kinetic Theory of Gases.

Our inequality may then be given in the form:

$$l > \frac{1}{3k} \frac{c}{u} \cdot L$$

The actual thickness of the wave front to be expected should not be smaller than the above value. We will find later that this is the case.

We will now proceed to study the differential equations of the wave front.

We write for equation III, Page 9.

$$c_p (T - T_1) + \frac{u^2 - u_1^2}{2g} - \frac{\lambda}{\gamma_1 u_1} \frac{dT}{dx} = 0 \quad \text{VI}$$

Let us find the properties of the inversion point on the temperature curve. Differentiation with respect to x gives:

$$c_p T' + \frac{u}{g} u' - \frac{\lambda}{\gamma_1 u_1} T'' = 0$$

or at the inversion point:

$$T' = - \frac{u}{g c_p} u' \quad \text{VII}$$

Substituting this in equation VI gives:

$$c_p (T - T_1) + \frac{u^2 - u_1^2}{2g} + \frac{\lambda}{\gamma_1 u_1} \frac{u}{g c_p} u' = 0$$

Letters without index will in the following refer to the inversion point of the temperature curve.

We have further from equation V:

$$RT - \left(\frac{\gamma_1 u_1^2}{g} + p_1 \right) \frac{u}{\gamma_1 u_1} - \mu \frac{u}{\gamma_1 u_1} u' + \frac{u^2}{g} = 0$$

Elimination of T gives:

$$\begin{aligned} \frac{c_p}{R} \left(\frac{\gamma_1 u_1^2}{g} + p_1 \right) \frac{u}{\gamma_1 u_1} + \frac{c_p}{R} \mu \frac{u}{\gamma_1 u_1} u' - \frac{c_p}{R} \frac{u^2}{g} = \\ c_p T_1 - \frac{u^2 - u_1^2}{2g} - \frac{\lambda}{\gamma_1 u_1} \frac{u}{g c_p} u' \end{aligned}$$

This gives as value for u' at the inflection point

$$\left(\mu \frac{c_p}{R} \frac{u}{\gamma_1 u_1} + \frac{\lambda}{\gamma_1 u_1} \frac{u}{g c_p} \right) u' =$$

$$c_p T_1 - \frac{u^2 - u_1^2}{2g} - \frac{c_p}{R} \left(\frac{\gamma_1 u_1^2}{g} + p_1 \right) \frac{u}{\gamma_1 u_1} + \frac{c_p}{R} \frac{u^2}{g}$$

$$\text{With } \frac{u}{u_1} = \omega \text{ and } T_1 = \frac{p_1 v_1}{R}:$$

$$\omega \left(\mu \frac{c_p}{R} + \frac{\lambda}{g c_p} \right) u' =$$

$$\frac{c_p}{R} p_1 (1 - \omega) - \frac{\gamma_1 u_1^2}{2g} (\omega^2 - 1) - \frac{c_p}{R} \frac{\gamma_1 u_1^2}{g} \omega (1 - \omega) =$$

$$\left(\mu \frac{c_p}{R} + \frac{\lambda}{g c_p} \right) \frac{\omega}{1 - \omega} u' = \frac{c_p}{R} p_1 + \frac{\gamma_1 u_1^2}{2g} \left(1 + \omega - \frac{2c_p}{R} \omega \right) \quad \text{VIII}$$

We know from relation VII that the velocity gradient has the opposite sign of the temperature gradient at the inversion point. We are studying a case where the temperature is increasing in the positive x direction. (See Fig. 2).

ω is then always < 1

The coefficient of u' in the final equation VIII is thus always positive, and since u' is negative this means that the right side of the equation must always be negative.

It is always so; although this is not immediately apparent.

We wish to bring our equation on a more symmetrical form:

$$\text{We divide the right side by } \frac{\gamma_1 u_1^2}{2g}$$

and obtain:

$$\frac{2c_p}{R} \frac{p_1 g}{\gamma_1 u_1^2} + 1 + \omega - \frac{2c_p}{R} \omega =$$

$$\frac{2c_p}{R} \left(\frac{c_1}{u_1} \right)^2 + 1 - \omega \left(\frac{2c_p}{R} - 1 \right) \text{ where } c_1$$

is the ordinary velocity of sound of small amplitudes. Introducing

$k = \frac{c_p}{c_v}$ the expression becomes:

$$\frac{2}{k-1} \frac{c_1^2}{u_1} + 1 - \frac{k+1}{k-1} \omega, \text{ and the equation VIII:}$$

$$\left(\mu \frac{c_p}{R} + \frac{\lambda}{gc_p}\right) \frac{\omega}{1-\omega} \cdot u' = \frac{\gamma_1 u_1^2}{2g} \left\{ \frac{k+1}{k-1} (1-\omega) - \frac{2}{k-1} \frac{u_1^2 - c_1^2}{u_1^2} \right\}$$

Developing $\frac{2}{k-1} \frac{u_1^2 - c_1^2}{u_1^2}$ in terms of w_0 , the final volume on

the Hugoniot curve, we obtain the value

$$\frac{k+1}{k-1} (1-\omega_0)$$

and as result:

$$- u' \Gamma \frac{\omega}{1-\omega} = \frac{\gamma_1 u_1^2}{2g} \frac{k+1}{k-1} (\omega - \omega_0)$$

where Γ refers to the bracket on the left side of the preceding equation and is a constant of the material.

We introduce again:

$$T' = - \frac{u}{gc_p} u'$$

and we obtain:

$$g c_p T' \frac{1}{u} \cdot \Gamma \frac{\omega}{1-\omega} = \frac{\gamma_1 u_1^2}{2g} \frac{k+1}{k-1} (\omega - \omega_0)$$

Defining a magnitude l as $T_2 - T_1 : T'_{\max}$

$$\text{We have with } T_2 - T_1 = \frac{u_1^2 - u_2^2}{2gc_p} = \frac{u_1^2}{2gc_p} (1 - \omega_0^2)$$

$$l = \frac{u_1^2}{2g} \frac{1 - \omega_0}{c_p T'_{\max}} =$$

$$\frac{u_1^2}{2} (1 - \omega_0^2) \frac{1}{u} \Gamma \frac{\omega}{1-\omega} : \frac{\gamma_1 u_1^2}{2g} \frac{k+1}{k-1} (\omega - \omega_0)$$

$$l = \frac{\Gamma}{\gamma_1 u_1} g \cdot \frac{k-1}{k+1} \frac{1 - \omega_0^2}{(1-\omega)(\omega - \omega_0)} = \frac{Cg}{\gamma_1 u_1} \frac{1 - \omega_0^2}{(1-\omega)(\omega - \omega_0)} \quad \text{IX}$$

$$\text{where } C = \frac{k-1}{k+1} \Gamma$$

We do not yet know the value of ω but it is the merit of the above method that we are easily able to obtain a *minimum value* of the expression for l . This minimum expression differs in fact very slightly from the actual value of l . Even for reasons of symmetry, we will admit that the temperature at the inversion point and the corresponding volume must be represented by a point somewhere near the middle between the two end points.

In this region, however, the expression IX fortunately has a nearly stationary value.

The minimum value of the expression: is seen to be equal to:

$$l > \frac{4 \text{ } Cg}{\gamma_1 u_1} \frac{1 - \omega_0^2}{(1 - \omega_0)^2} = \frac{4 \text{ } Cg}{\gamma_1 u_1} \frac{1 + \omega_0}{1 - \omega_0} \quad \text{X}$$

Introducing the pressure ratio $\frac{p_2}{p_1} = \pi_0$

we obtain the equivalent form:

$$l > 4k \frac{Cg}{\gamma_1 u_1} \frac{\pi_0 + 1}{\pi_0 - 1} \quad \text{XI}$$

This is a general relation for the thickness of the wave front. The inequality is very weak. We are not thus depending on any special

values of the ratio $\frac{\lambda}{c_v \eta}$ as in the case of Becker's special expression (p 344 Z. f. Ph. Bd. 8).

If we restrict the use of the formula to comparatively small values of π_0 the result becomes correct in an absolute sense, that is: all the conditions imposed through the differential equations III and IV are fulfilled with any desired accuracy. In particular, the friction and

heat conduction will become equal to $\mu \frac{du}{dx}$, and $\lambda \frac{dT}{dx}$ respectively.

The specific heats c_v and c_p and the ratio k may also be regarded as constants. The result may be applied to any (nearly) perfect gas.

The following table gives a few representative values of l for air as obtained under the assumptions made.

The value of C is for air $1.7 \cdot 10^{-6} \text{ } kgm \cdot sec.$

γ is put equal to $1.3 \text{ } kgm$

TABLE I

π_0	1.01	2	10	100	2000	
u_1	332	492	978	3020	12900	$m \text{ sec}^{-1}$
l	44600	435	89	24	5.5	10^{-7} cm

The imposed conditions are probably fairly well satisfied for disturbances with a pressure amplitude less than about 10 atm. in air.

Beyond this point we are strictly speaking, no longer allowed to put the friction equal to $\mu \frac{du}{dx}$ etc., since the thickness of the layer becomes less than the mean free path.

III. DISCUSSION OF THE RESULTS

We know from the classical theory of sound that if we consider waves of a definite amplitude, there exists a tendency for the wave front to become steeper.

There is nothing in the preceding developments that prevents us from applying our results on small disturbances. Since the formula giving the minimum value of l , contains no approximations, we are justified in using it for the limiting case π_0 approaches 1. We obtain some interesting conclusions.

We write for small values of $\pi_0 - 1 = \Delta\pi_0$ and we have

$$l > \frac{8kCg}{\gamma c_1} \frac{1}{\Delta\pi_0} \text{---Where } c_1 \text{ is the velocity of sound.}$$

For $\Delta\pi_0 = 1/100$ we have from Table 1:

$$l = 44600 \cdot 10^{-7} \text{ cm.}$$

For $\Delta\pi = 1/1000$ we obtain:

$$= 446000 \cdot 10^{-7} \text{ cm or about } 1/20 \text{ cm,}$$

that is: disturbances corresponding to ordinary physiological waves take on a wave front of about $1/20 \text{ cm}$ in air.

We know that the general effect of friction and heat conduction is to decrease existing velocity and temperature gradients.

On the other hand, we have indicated that the disturbance possesses an inherent property of increasing the same magnitudes in the front.

The two effects consequently have a tendency to cancel each other in the *front* of the disturbance, while they always add up in the *rear* of the disturbance.

Let us in the following use the temperature gradient as a representative parameter of the disturbance, so as to avoid repetitions regarding the effects on the velocity and pressure gradients.

The results obtained in the preceding refer strictly to a case in which a single disturbance must be considered to extend from the negative to the positive infinity.

The Hugoniot equation gives a relation between the state point "before" and the state point "after" the disturbance. These two points are then, strictly speaking, located infinitely far apart.

It is, however, obvious that we may approach the center of the disturbance to a distance of a few times l without causing any appreciable deviation from our relation. The gradients of the temperature and the velocity decrease rapidly with the distance from this center.

That is, we may consider two points, located rather close to the center of the disturbance, as being connected through the Hugoniot relation, and we are not directly interested in what takes place beyond these points. We know, on the other hand, from the general theory of large waves that the only "permanent" form of such waves is where the final step front has been reached. The form is however, not absolutely permanent since, obviously, the amplitude must decrease due to frictional effects. The thickness of the front will apparently increase correspondingly. The essential thing to note is, however, that these changes in the form of the disturbance may be regarded as "slow", at least in certain cases.

The form of the wave is for instance more stable or permanent if the wave length is large. We will see later that the disturbance apparently persists longer in this case.

We will for such a case apply the Hugoniot relation although we are aware of the fact that the mathematical stringency of our analysis is lacking to some extent.

Let us create a very powerful disturbance in the form of sine waves. The magnitude l as defined above will now have the initial

value $\frac{\lambda}{\pi}$ — where λ is the wave length. It will, however, very rapidly

reach the "equilibrium value" $\frac{4Cg}{\gamma_1 u_1} \frac{1+w_0}{1-w_0}$.

Any further increase in the steepness is impossible, since from here on the effect of friction and heat conduction, that is the effect of decreasing the gradient, is in excess.

The very steep front, representing the final state of the disturbance causes a large increase of entropy in the medium on passing through the front. This increase of entropy should, however, be of the same order whether the front has reached its final state or not. The effect of the larger gradients is approximately cancelled by the inversely decreased time of passage through the front.

In any case we are able to calculate accurately this increase in entropy or the corresponding heating effect, caused by the front of the disturbance, in the case where the final stage is attained.

Let us now proceed to discuss the case where the amplitude of the disturbance is infinitely small. We have showed that in this case the wave front is infinitely thick. This apparently very peculiar result comes about in the following manner:

The effect of friction and heat conduction now dominates the situation. Waves of a small but definite amplitude will in general possess a gradient which is even greater than the equilibrium gradient.

It is obviously quite possible to *create* waves which are steeper than the corresponding equilibrium form. Since there must exist a tendency to decrease the gradients in the front, we can see that this is equivalent to the fact that the effect of friction and heat conduction is in excess.

IV. DISCUSSION OF THE VALIDITY OF THE DIFFERENTIAL EQUATIONS OF THE WAVE FRONT

There is *a priori* an obvious lack of preciseness in the quantities defining temperature and pressure. No Maxwellian velocity disturbance can be expected and there is no reason to expect that the energy is evenly divided among the various degrees of freedom.

Suppose, however, that we have a special process able to furnish us with certain scalar quantities capable of replacing what we have previously called temperature and pressure. The equation III and IV should then be correct, but p and T would differ in value from their thermodynamical (equilibrium) values.

Provided we are able to discover the above process we shall expect to obtain a unique and correct answer.

Briefly: We state that equation III and IV are correct if we follow a flexibility in T and p .

The difficulty is now, however, that we are no longer at liberty to make *the transition IV to V* because p and v are no longer connected in this simple manner. The equation $p v = RT$ is only true for thermal equilibrium: In fact, this relation does not any more equate scalar quantities. It is perfectly possible to have the pressure different in different directions. It is also possible to imagine a temperature which varies in magnitude with the direction, even if a precise definition of temperature in this case might be difficult.

We will in the following indicate how this effect must be expected from the view point of the kinetic gas theory:

Assume we have a cylinder, infinitely large in diameter compared with the length. Let it contain a highly rarified diatomic gas at high temperature. Let the gas be in thermal equilibrium.

Let us next compress the gas by moving a piston at high rate of velocity. Our object is, in other words, to nullify the probability of

impacts between the molecules themselves and between the latter and the cylindrical wall. Let the axis of the cylinder be in the x -direction, Fig. 5.



FIG. 5

What happens is the following:

The energy supplied from the piston will be absorbed exclusively: as x — component of velocity, as rotation about y and z axis and as vibration in direction x . There will be no energy absorbed by the y and z components of velocity, no increase in rotation about the x — axis, nor any increase in vibration perpendicular to same. This means that the energy, initially, is received by:

$$\left. \begin{array}{l} 1 \text{ translational} \\ 2/3 \text{ rotational} \\ 1/3 \text{ vibrational} \end{array} \right\} \text{degrees of freedom,}$$

or one-half only, of the total increase is received by the translational degrees of freedom.

After a certain lapse of time, however, this fraction will approach $3/5$, the equilibrium value.

We can now see that the equations III and IV are misrepresentative of the actual situation. The p occurring in equation IV is the *pressure in the x direction*; while the T occurring in equation III stands for the *energy in one place* and for the *temperature in the x direction* in the other place.

Let us confine an element of our gas between two weightless membranes located parallel at a distance ax . On passing through the wave front the gas would be subjected to a rapid compression in the direction of propagation, and we must expect an effort similar to the one described above.

That is: The temperature and the pressure in the x — direction will both be larger than the "averages". It is important to notice that the thickness of the wave front is of the order of the mean free path and decreases rapidly with increase in pressure.

The above analysis is, however, still more interesting in connection with the question of detonations of chemical nature, as there does not

seem to exist any satisfactory explanations of the extreme rapidity of such reactions. We are able to draw an important conclusion.

Let us postulate, what is highly probable, that the most important factor in such reactions is the translational energy in the direction of propagation. We know that in equilibrium this energy is only *one-fifth* of the total for diatomic gases and even less if there are more atoms in the molecule. Apparently there is a tendency to absorb in the limit *one-half* of the total energy by the component in question. How much there is really absorbed is difficult to determine, but we must admit that the more rapid the combustion is, the *more* we may expect this effect.

The effect is equivalent to an *excess* of "temperature" in the x — direction which is rapidly increasing in importance with the magnitude of the disturbance. Although the ordinary definition of temperature here is completely lost, we may still use the expression as an indication of the force of the reaction.

V. DEDUCTION OF AN APPROXIMATE RELATION FOR THE DISSIPATION OF ENERGY IN NOISE.

It is a known fact that noise or comparatively large disturbances decrease in intensity relatively faster than ordinary sound waves. The noise, in order to give any appreciable physiological effect, must obviously carry quite an amount of energy per disturbance as compared with sound waves. Hence we may consider noise as (comparatively) small detonations. We limit as usual our study to plane disturbances.

It may be seen from our earlier considerations of the thickness of the wave front, that any violent disturbance must rapidly assume the final form, that is—the step front.

Let us neglect any increase in entropy in rear of the maximum amplitude; in other words we assume that the entire decrease of availability of the energy takes place in the front of the disturbance. We consider only small amplitudes Δp or ΔT . These amplitudes are assumed to be large, however, compared with those of sound waves. It may be seen from the following development that no appreciable error is introduced for values of Δp equal to or less than $0.1 p$.

The wave front is thus, in all cases, what we may call "vertical".

Let T_1 be the temperature of the medium ahead of the disturbance.

The maximum temperature T_2 is then given by the following relation, obtained from the Hugoniot equation:

$$\frac{T_2}{T_1} = \pi_0 \frac{\pi_0 + \xi}{\pi_0 \xi + 1} \quad \text{where } \xi = \frac{2c_v}{R} + 1$$

We will restrict our problem to air, and we have $\xi = 6$. We have then for small amplitudes:

$$1 + \frac{\Delta T}{T_1} = \left(1 + \frac{\Delta p}{P_1}\right) \frac{1 + \frac{\Delta p}{p_1} + 6}{6\left(1 + \frac{\Delta p}{p_1}\right) + 1}$$

$$\frac{\Delta T}{T_1} = \frac{2}{7} \frac{\Delta p}{p_1} \cdot \frac{1 + \frac{1}{2} \frac{\Delta p}{p_1}}{1 + \frac{6}{7} \frac{\Delta p}{P_1}}$$

$$\frac{\Delta T}{T_1} = \frac{2}{7} \frac{\Delta p}{P_1} \left(1 + \frac{1}{2} \frac{\Delta p}{p_1}\right)$$

$$\left(1 - \frac{6}{7} \frac{\Delta p}{p_1} + \frac{6^2}{7^2} \left(\frac{\Delta p}{p_1}\right)^2 - \frac{6^3}{7^3} \left(\frac{\Delta p}{p_1}\right)^3 + \dots\right)$$

$$\frac{\Delta T}{T_1} = \frac{2}{7} \frac{\Delta p}{p_1} \left\{ 1 - \frac{5}{14} \frac{\Delta p}{p_1} + \frac{15}{49} \left(\frac{\Delta p}{p_1}\right)^2 - \frac{90}{7^3} \left(\frac{\Delta p}{p_1}\right)^3 + \frac{108}{7^3} \left(\frac{\Delta p}{p_1}\right)^4 - \dots \right\}$$

Let us consider an isentropic compression of small amplitude in the same manner.

$$\frac{T_2}{T_1} = \pi_0^{\frac{k-1}{k}} = \pi_0^{\frac{2}{7}} = \left(1 + \frac{\Delta p}{p}\right)^{\frac{2}{7}}$$

or developed:

$$\left(\frac{\Delta T}{T_1}\right) = \frac{2}{7} \frac{\Delta p}{p_1} \left\{ 1 - \frac{5}{14} \frac{\Delta p}{p_1} + \frac{10}{49} \left(\frac{\Delta p}{p_1}\right)^2 - \frac{95}{2 \cdot 7^3} \left(\frac{\Delta p}{p_1}\right)^3 + \dots \right\}$$

The difference between the two expressions becomes:

$$\frac{\Delta T}{T_1} - \left(\frac{\Delta T}{T_1}\right) = \frac{\Delta \Delta T}{T_1} = \frac{2}{7} \frac{\Delta p}{p_1} \left\{ \frac{5}{49} \left(\frac{\Delta p}{p_1}\right)^2 - \frac{85}{2 \cdot 7^3} \left(\frac{\Delta p}{p_1}\right)^3 + \dots \right\}$$

If we only retain members of the lowest order for the expression $\Delta \Delta T$ and ΔT we obtain:

$$\frac{\Delta\Delta T}{\Delta T} = -\frac{5}{4} \left(\frac{\Delta T^2}{T_1} \right)$$

The symbol $\Delta\Delta T$ denotes the difference of the two ΔT s, which is obvious from the preceding. In accordance with our assumption this magnitude gives the temperature rise in the medium due to the passage of the disturbance. The quantity ΔT on the other hand is a measure of the energy of the disturbance. We put this energy proportional to $\Delta T \lambda$ where λ is a length comparable to the dimension of the disturbance in the direction of propagation.

In order to facilitate a more precise definition of this term, we will restrict the following application to a *series* of disturbances, as for instance of the type produced by a machine gun or an air hammer. The appearance of such "waves" is indicated in Fig. 6.

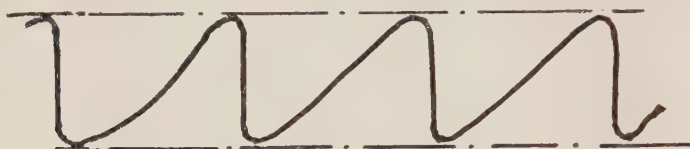


FIG. 6

The energy of each "wave" may now as a first approximation be considered proportional to the product of the amplitude ΔT and the distance between the "waves".

λ is consequently considered equal to this distance. This result comes about by comparison with a wave of "normal" shape. In order to comply with our initial assumption of no loss in the rear of the wave, we shall obviously restrict our case to larger values of λ .

The left side of the above expression may consequently be propounded as the relative decrease of the energy or the temperature amplitude of the plane disturbance when this is propagated through a distance λ .

Let us express the temperature amplitude in terms of T_1 , the temperature of the medium. That is, we let $a = \frac{\Delta T}{T_1}$ represent this amplitude.

We may write for the plane disturbance:

$$\frac{d\alpha}{\alpha^3} = -\frac{5}{4} \frac{dx}{\lambda}$$

or integrated

$$\alpha = \frac{1}{\sqrt{\frac{5}{2} \frac{x}{\lambda} + \frac{1}{\alpha_0^2}}}$$

Where a_0 is the amplitude at $x = 0$.

This result is interesting. It explains, in a general way, why noises which near their point of creation are "terrible" softens off relatively quickly. Although the formula only is correct for comparatively small plane disturbances, it is able to yield some general information as to the dissipation of ordinary disturbances of large amplitudes. We see that at a large distance x , the amplitude depends very little on the initial amplitude as indicated above. We observe further that the amplitude persists longer if λ is large, that is if the frequency is lower. This result is in agreement with experiments by D. C. Miller.*

*See Handbuch der Physik Bd VIII bottom of page 652 and top of page 653: Experiments by D. C. Miller.

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ON THE COMBUSTION OF OIL

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS
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INTRODUCTION

This report contains the data obtained from experiments on different types of Oil Burners. These experiments were conducted in the Mechanical Laboratory of the Johns Hopkins University in Baltimore, Maryland. The main object of the investigation was to make a generalized study of the process of burning oil in a small boiler under varying conditions, particularly in order to determine common characteristics and to obtain information of general applicability.

While the oil burner for years has been giving excellent service in large plants, its adaption for the use in small boilers represents a problem of a much more complicated nature. The difference is entirely due to the dimensions involved. A large furnace of almost any practical design is always capable of consuming the oil injected into it by any proper mechanical device. Only conspicuous deficiencies are able to interfere with the proper combustion of the oil. The burner itself is almost immaterial, as far as combustion is concerned, because sufficient time and space is available for its progress and completion in the furnace.

Here is where the difficulties arise as regards the small domestic type of boiler. Arbitrary combinations of burners and boilers are a priori not permissible. The state of perfection of the burner attains vital importance. The burner must be able to deliver the fuel in a condition capable of almost instantaneous combustion. If this end is not achieved a more or less incomplete combustion will inevitably result.

The time allowed for combustion is very short and any possible means of assisting it is of value. The proper design of the furnace becomes an important factor. This problem is not an easy one, as even the mere definition of a most desirable condition will cause considerable difficulties. It must be remembered that the chemistry of combustion of hydrocarbons both gaseous and catalytic, notwithstanding serious efforts, largely is a "terra incognita"* neither is any useful information available on the radiation from hydrocarbon flames. Even the question of soot formation may be subject to serious discussion although several facts are known. The present investigation is merely an effort to represent facts regarding the combustion and associated questions. No consideration is given to commercial or other viewpoints not directly involved in the questions examined, nor is any attention being paid to purely mechanical aspects of the problem. The results of the investigation are shown in the tables and diagrams at the end of this paper.

See: W. A. Bone: "Flame and Combustion in Gases," Longmans, Green & Co., London 1927.

I. SCOPE OF INVESTIGATIONS.

The following is a statement of the problems more or less extensively covered by experiments and theoretical considerations.

1. Study of the general nature of the products of incomplete combustion.

2. Study of the influence of the oil-air ratio on the completeness of combustion.

3. Study of the influence of a cold start, intermittent operation or generally expressed: The action of the instantaneous furnace temperature on the completeness of the combustion.

4. Study how the losses due to incomplete combustion vary in different combinations burner-boiler.

5. A study of the relation of the carbondioxide and oxygen in the products of combustion, and the use of graphical methods in connection with oil burner testing.

6. Study of the heat absorption of the boiler as depending on the excess air and rating.

7. Study of the action of the heat capacity of the furnace and boiler in starting and intermittent operation.

8. Influence of the oil on the combustion.

The obtained data will in the following, as far as possible, be handled in this order. Enough theoretical data will be included as are necessary for a complete representation of the material.

II. METHODS OF CONDUCTING TESTS.

A large part of this investigation consists of ordinary boiler tests.* These were, however, run in a special manner in order to obtain the greatest possible reliability and accuracy.

The problem of technical testing is often an extremely complicated one due to the large number of variables usually involved. It is useful and some times essential to simplify the problems and methods of testing. Any available method of checking should be employed. The complete heat balance of a test thus gives valuable information on the accuracy attained. It is also essential to eliminate as far as possible any sources of error. One of these is for instance the great time lag between output and input of heat in the boiler, caused by the capacity of the furnace and boiler. While the latter item, the heat capacity of the boiler and its water content is relatively small, the former may reach quite large values. The fig. 6 later referred to, shows for instance that the equilibrium condition is not reached in 3 hours after start! Any boiler test run on this boiler with less than three hours previous heating up, is thus bound to show too low values of the efficiency. While the heat capacity of the boiler proper and its water content can be figured with any desired accuracy, the calculation of the heat capacity of the brick lining involves the assumption of an average temperature. The rate of heat transfer from the furnace and the conductivity of the bricks however have to be known. This latter

* I wish to express my heartiest thanks to Mr. G. H. Dew, senior student of this university for valuable assistance with these tests.

problem is though of too little direct interest to be submitted to individual approximate solutions, and the proper procedure is to actually measure the instantaneous output from the boiler. How this was done will be shown in the following. Also see figs. 2 and 7.

Another source of error is the heat radiation from the boiler proper. One way to eliminate this would be to use a "perfect" insulation.—A method used successfully in connection with simple bodies, for example, pipes, is electric compensation. That is the outward heat flow is stopped and the radiation loss furnished by electric energy.—The method used here was to keep the boiler almost at room temperature. The remaining radiation from doors, etc., is then small enough to be estimated with accuracy.—For above reasons it was found useful to run the boiler as an ordinary Junker calorimeter. City water was furnished to the boiler at a rate so as to allow a temperature rise of about 50-60 degrees F. The inlet pressure of the water was measured on a mercury u-tube manometer and the rate of flow kept within very narrow limits by hand regulation. It was passed from the boiler alternately to each of two Howe test scales of 8000 lbs. capacity, where it was weighed.

An ordinary Orsat of an accurate make was used on the job for instantaneous determinations of the CO_2 and O_2 contents of the flue gas. This latter reading was however soon omitted as being superfluous for reasons later explained. A large gas sampling bottle initially filled with a saturated Na Cl (common salt) solution was used to collect an average sample for complete analysis. This bottle was "started" when the desired condition of the boiler was reached. That is, the confined liquid was allowed to escape while the gas was drawn in at the top of the bottle. The rate of flow was so adjusted as to extend the sampling over the period desired. A few instantaneous samples were also collected as a further assurance against accidental errors.

The stack temperature was measured with ordinary high temperature mercury thermometers, one placed inside the smoke box and one in the stack about ten inches apart from it in direction of the gas travel. This double reading gives a good indication of the magnitude of existing errors. The possible error from this source is quite small however. A 50°F difference in the stack temperature corresponds to only about 1% of the gross heat value, and this is already within the error limits of a most accurate test.

The temperature in the middle of the first flue of the boiler was also measured in a large number of tests. This was done by means of a Cromel-P vs. Alumel thermocouple connected to a Northrup millivoltmeter. The couple was properly protected against radiation by a cylindrical shield. This temperature was measured in order to obtain information on the rate of heat transmission in the flues, and was thus indirectly used as a "soot indicator".

It will be noted that a certain number of the boiler tests were run so as to include the entire period from the starting of the burner to the

point where the initial condition of the boiler was practically restored after cooling. As shown later, these tests furnish a far more complete information about the unit burner-boiler than can possibly be obtained by the ordinary equilibrium test. This of course with particular reference to intermittent service. Such tests will be referred to as complete tests, merely indicating that starting and cooling periods have been included. Diagrams 2 and 7 show samples of this type. One ordinary intermittent operation test (Fig. 8) and a number of equilibrium tests were also performed.

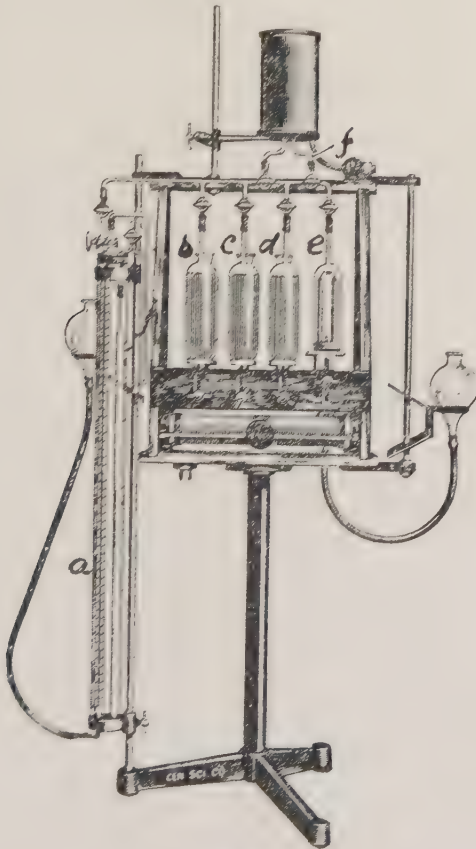


FIG. 11

A few tests were run exclusively in order to study the combustion loss from a cold start. Diagram 12 shows in graphical form a representative test of this type. The procedure was as follows:

The burner and dampers were left as adjusted from a previous run. The furnace was allowed to cool down to room temperature. The test was in fact usually run on a day following the ordinary test and as a repetition of same. The burner was then started and snap samples collected after any desired lapse of time from the start. The samples

were then subjected to complete analysis on the Burrell Orsat. The furnace was again allowed to cool down the same procedure was repeated until the desired number of samples had been obtained.

Since the loss due to incomplete combustion was one of the main objects of this investigation, a brief description of the particular instrument used for the determination of the products of incomplete combustion may be of interest. As mentioned before this was a Burrell type Orsat, also referred to as a Bureau of Mines Orsat. Fig. 14 gives an idea of its appearance. The gas sample is here drawn into the measuring burette (a). This is graduated to 0.1 cc., filled with mercury and equipped with a compensating tube (j). A caustic potash pipette (b) is employed to absorb the CO_2 in the usual manner. The pipette (c) containing fuming sulphuric acid is used to absorb the unsaturated hydrocarbons. Oxygen is then removed with pyrogallol in pipette (d). Tube (f) contains copper oxide, which is used as catalyst for selective, low temperature oxydation of the carbon monoxide and hydrogen. These are burned to carbon dioxide and water respectively at 300°C , while the paraffin hydrocarbons are not oxidized. These latter are then finally determined by slow combustion over a yellow-hot platinum spiral in pipette (e).

This instrument is particularly adapted for precision work and the manipulation requires a great deal of care. A single determination of a sample can hardly ever be relied on because of the great possibility of more or less accumulated errors. It was found necessary to perform two or three parallel determinations in order to obtain reliable results. A certain check was always at hand in the snap samples earlier mentioned. For a more detailed description and theory of the instrument see "Gas Chemists Handbook".[†]

The time needed to obtain one complete gas analysis including the paraffins is about one hour and a half, depending to some extent on the skill of the operator. It is thus entirely out of question to use this instrument on "The job", as the time element prohibits such practice. The apparatus is a typical laboratory instrument and can not be used to replace the ordinary portable Orsat in the boiler room. Some method of gas sampling is consequently needed as an intermediate link. It is a well known fact that carbon dioxide is absorbed rapidly in pure water. Also the oxygen content of the sample may be affected, depending on the air content of the confining liquid. Certain precautions must thus be observed, whenever a gas sample is collected over water. One method recommended is to saturate the water with common salt (NaCl), which method was found to be quite satisfactory. The liquid was also "saturated" with the gas, by pumping it through vigorously for some time previous to starting. This saturation process is however apparently quite slow and there is also a danger of some change in the gas composition throughout the test. It was found that even if these precautions were observed, there was an appreciable change in the sample if taken 24 hours apart from the same bottle. This however, does not apply to the products of incomplete combustion, which

[†] Published by the American Gas Association 130 East 50th Street, N. Y., see pp. 153.

fortunately remain unchanged within the error limits of the Orsat. As these were of main importance the following method was then adopted: The CO_2 and O_2 contents of the sampling bottle were in all cases considered identical with those obtained by direct determination on the job, and the necessary corrections applied when deviations occurred. The direct instantaneous readings on the portable Orsat were taken every ten minutes during the period of testing.

III. METHODS OF CALCULATION AND OTHER THEORETICAL INVESTIGATIONS.

The methods used in calculations of heat balance, excess air, etc. are slightly different from the ordinary due to the complication caused in considering the incomplete combustion. Errors involved in using conventional formulas are by no means small. It will be shown in the following that there are considerable amounts of unsaturated hydrocarbons and hydrogen in the combustion products.

Formulas based on the assumption that carbon monoxide is the only combustible constituent of the stack gas are thus in cases entirely misleading. A large percentage of the heat of the fuel cannot be accounted for, and the amount of excess air will be entirely too high.

Test 14, table 1, is thus an interesting, although somewhat drastic, example of the magnitude of possible deviations. The appearance of the flame and the conditions in general in this test would entirely have justified an estimation of the excess air to about 10 per cent, as the CO_2 content also seemed to indicate; however the complete analysis showed that the test had been run at an air-deficiency of not less than 12%. The apparent excess air based solely on the CO content was in fact 7% or about 19% too high. No soot whatsoever was produced in this test apparently due to a very special bricking of the furnace.

CALCULATION OF HEAT BALANCE

(a) Useful heat:

The instantaneous value of the heat absorbed by the boiler is obtained directly as product of water weight and temperature difference:

$$H = W \Delta t \frac{\text{Btu}}{\text{lbs.}} \quad \text{where } W \text{ is the lbs. of cooling water per lb. of oil}$$

fuel, and Δt is the temperature increase across the boiler due to absorbed heat.

(b) Dry stack loss:

This is obtained by the following formula:

$$D = \frac{C_{p\text{CO}_2} \cdot \text{CO}_2 + C_{p\text{H}_2\text{O}} (100 - \text{CO}_2)}{\text{CO}_2 + \text{CO} + n C_n h_{2n}} \frac{\Delta T}{12} \frac{\text{CO}}{\text{lb}} \frac{\text{BTU}}{\text{lb}}$$

where:

D = Dry stack loss.

ΔT is stack temperature minus room temperature.

C_p is the average specific heat per lb.—mol for the temperature range in question.

C_o is the per cent by weight of carbon in the oil.

CO_2 , CO and $C_n h_{2n}$ represent per cent by volume of carbondioxide, carbonmonoxide and hydrocarbons respectively in the dry sample.

Because the molecular specific heat of the unsaturated hydrocarbons $C_n h_{2n}$ is even greater than that of the carbondioxide, these should preferably be included in the CO_2 of the nominator. The difference is however negligible.

The loss due to initial moisture in the combustion air is also conveniently included here. The average molecular specific heat is slightly over 8.0 for the possible range and the percentage by volume reaches 3.0 only in case of a very hot and moist day. The product Vc_p thus in no cases exceeds 25.0 and is usually less than 10.0, based on 60 F. and 50% humidity. This amount should be added in the nominator.

(c) Stack loss due to water of combustion:

It is customary in this country to base the boiler efficiency etc. on the higher or gross heat value of the fuel. For this reason the entire heat content of the water produced in combustion is to be considered as a stack loss.

The amount of available or free hydrogen in the fuel is $h_o\%$ by weight. This gives a total amount of $9h_o$ lbs. of combustion water per lb. of oil, which is a maximum value, corresponding to complete combustion. The resulting partial pressure of this water-vapor is less than 2 lbs. per square inch, and the heat content thus fairly independent of the pressure. At an average case of 550° F. stack temperature this heat content is 1312 Btu. For 60° F. room temperature, we get:

$$H_2 O\text{-Loss} = 9h_o (1312-28) = 11500 h_o \frac{\text{BTU}}{\text{lb.}}$$

This is a close approximation; for accurate work the unburned hydrogen must be considered, which results in a slightly lower value of the H_2O loss.

(d) Loss due to incomplete combustion.

The following heat values are used:

$H_2 + \frac{1}{2}O_2 = 103530$ BTU per lb. mol. Low.

$CO + \frac{1}{2}O_2 = 122130$ — per ———

$C_2 H_4 + 3O_2 = 575370$ — per ——— Low.

(See University of Illinois Bulletin No. 139)

Incomplete combustion loss:

$$\frac{103530 H_2 + 122130 CO + 575370 C_n h_{2n}}{12 (CO_2 + CO + n C_n h_{2n})} \frac{\text{BTU}}{\text{lb.}}$$

Lower heat values are used here, because the vapor loss is included in (c). The heat value of ethylene is used for the unsaturated hydrocarbons.

GRAPHICAL GAS ANALYSIS AND CALCULATION OF EXCESS AIR.

To those who are not familiar with the use of the Ostwald combustion-diagram, a brief description will be given,—as a large benefit is derived from this in practical boiler testing. It is of particular value in the case of uniform fuels, i. e. oils. Fig. 1 shows an Ostwald combustion triangle. The carbon dioxide is plotted as ordinate against the oxygen as abscissa. Any arbitrary gas composition is consequently represented by a definite point in this diagram. It can be proved that the locus of points corresponding to perfect combustion, forms a straight line a-b. This line connects the points ($\text{CO}_2 = \text{max}$, $\text{O}_2 = 0$) and ($\text{CO}_2 = 0$, $\text{O}_2 = 20.9$). $\text{CO}_2 = \text{max}$ is the theoretical maximum of the carbon dioxide, corresponding to complete combustion at 0% excess air. How this value is determined will be found in textbooks on combustion. It depends solely on the carbon-hydrogen ratio of the fuel. Throughout these tests a value in the close neighborhood of 15.2 was repeatedly verified. The magnitude should correctly be determined by a chemical analysis of the oil. Above figure corresponds however

1
to a ratio of 84 to 13.4 = $\frac{1}{0.159}$ — which value is apparently very nearly

realized in the average grade of oils used for domestic purposes.

The Ostwald diagram was originally worked out for the assumed case that carbon monoxide was the only product of incomplete combustion. Each value of CO is represented by a straight line parallel to the line of complete combustion and below it. If a test point was found to fall below the line a-b the combustion must be incomplete and the amount of CO can be read directly off the diagram. The writer has been using the Ostwald diagram for several years in connection with coal burning boilers, and invariably found it to be of great assistance in indicating incomplete combustion and as a means of checking the Orsat readings.

When the present study of oil burners was taken up, it was found however that the combustion point when plotted on the graph, curiously enough would *always* fall on the line a-b, no matter how imperfect the combustion happened to be. In other words, the amounts of O_2 and CO_2 in the products were identical with those to be expected in complete combustion. Even if the excess air was cut down to a negative amount this was still substantially true. Several explanations were resorted to, but it was not until the problem was subjected to a theoretical analysis based on the information obtained in the meanwhile, that the correct solution was found. This analysis will be developed in the following. Several important conclusions can be deduced from it and it also yields an indirect verification of various other data. The result is of practical value in testing.

This problem is:

Give a mathematical relation between the various gaseous constituents in the products of combustion.

Conditions:

The gas consists only of the following products in per cent by volume of lb. mols: Nitrogen N_2 , Oxygen O_2 , Hydrogen H_2 , Carbon dioxide CO_2 , carbon monoxide CO and unsaturated hydrocarbons $C_n h_{2n}$.

Let us designate the hydrogen-carbon ratio of the oil (by weight) as h_o
 $\frac{H}{C} = x$. Referring to an arbitrary gas sample we get:

$$C = 12 (CO_2 + CO + n \cdot C_n h_{2n}) \text{ as carbon, and}$$

$$H = 2 (H_2 + H_2O + n \cdot C_n h_{2n}) \text{ as hydrogen,}$$

where both are given in weight units.

$$\text{and further } \frac{H}{C} = \frac{1}{6} \frac{H_2 + H_2O + n \cdot C_n h_{2n}}{CO_2 + CO + n \cdot C_n h_{2n}}$$

which ratio is identical with that of the fuel x . Becomes this ratio

$$\frac{H}{C} \text{ respectively } \frac{h_o}{C_o} \text{ is always close to } 1/6, \text{ it is seen that the above}$$

fraction $\frac{H_2 + H_2O + n \cdot C_n h_{2n}}{CO_2 + CO + n \cdot C_n h_{2n}}$ is close to unity. The amount of unsaturated hydrocarbons is small and the following simplification is permissible:

$$\frac{H}{C} = \frac{1}{6} \frac{H_2 + H_2O}{CO_2 + CO} = x$$

We get from this relation

$$1. \quad H_2O = 6x \cdot (CO_2 + CO) - H_2$$

This amount of water vapor does not exist in the sample as analyzed, nevertheless it is produced from the hydrogen in the oil. We will now make use of the following consideration: As the entire quantity of oxygen and nitrogen in the sample is furnished by the air, the two fractions still exist in a ratio identical to that of the air. (including the condensed water vapor.) In per cent by volume or lbs.-molecules:

2. $N_2 = 3.78 (O_n + O'_2)$ where O'_2 means burned oxygen, and is obtained as follows:
3. $O'_2 = CO_n + \frac{1}{2} CO + \frac{1}{2} H_2O$. The nitrogen is obtained by difference:

4. $N_2 = 100 - (O_2 + CO_2 + CO + H_2 + C_n h_{2n})$ and we get finally by means of equations 1, 2, 3, and 4 the important relation:
5. $O_2 + CO_2 (1 + 2.37.x) + CO (0.605 + 2.37.x) - 0.186 H_2 + 0.21 C_n h_{2n} = 20.9$ with the factors in per cent by volume.

If all the components included in this equation are actually determined by analysis this relation must hold true. It is essential to note that the co-efficients of H_2 and $C_n h_{2n}$ are quite small and of opposite sign. As their absolute amounts also happen to be small, it is obvious that the two last members of the equation (5) may be left out entirely. If, for example, the hydrogen = 0.8% and the illuminants = 0.4% which represents a very imperfect case of combustion the error involved is only $-0.186 \cdot 0.8 + 0.21 \cdot 0.4 = -0.065$ or less than one tenth of one per cent.

As this particular kind of combustion furthermore yields negligible amounts of carbon monoxide it will be noted that also the CO-member may be omitted from equation (5), notwithstanding its greater co-efficient. As seen elsewhere in this report the percentage of carbon monoxide seldom exceeds 0.2, and the total error caused in neglecting the last three members of equation (5) is: $1 \times 0.2 - 0.065 = 0.135$ or still of the order of one tenth of one per cent.

Special attention is here called to the fact that the *co-efficient* of CO is not negligible, being about 1. If any appreciable quantity existed in the particular case, this fact would be shown clearly in the Ostwald diagram. The combustion point will in this case fall below the line of perfect combustion. As this is not ordinarily the case we may inversely conclude that the quantity of carbon monoxide is small. The only assumption necessary for this conclusion is that equation (5) completely represents the actual conditions. As seen elsewhere large amounts of CO could be obtained only at conditions of appreciable air deficiency. The combustion point falls in this case below the "perfect" line and yields a quantitative verification of equation (5).

We have thus furnished satisfactory reasons why the combustion point always indicates a perfect combustion and knowing these we can make the following statements:

1. The ordinary Orsat is of no use on the job, except a CO_2 -meter.
2. It is entirely useless to measure the O_2 as this may be obtained from the Ostwald diagram.
3. No idea whatsoever can be obtained as to the completeness of the combustion by the ordinary Orsat.

Above statements are of fundamental importance in testing of oil burners. It would be desirable to verify however that all eventualities are covered.

The apparent contradiction mentioned above is thus explained. The following abbreviation of equation (5): $O_2 + CO_2 (1 + 2.37x)$

≈ 20.9 is correct within the error limits of the Orsat. This equation is identical with the line of perfect combustion shown in fig. 1. where x is inserted as 0.159 and we get: $O_2 + 1.377 CO_2 = 20.9$ as a universal relation for the fuels in question.

CALCULATION OF EXCESS CO-EFFICIENT

The ordinary assumption that CO is the only loss is as mentioned previously, no longer correct, and a special calculation is necessary in order to obtain the excess air. The errors caused in using approximate formulas, based on the CO only, are by no means small, and only a rough estimate of the excess air can be gotten in this manner.

Using the previous nomenclature, we have for the excess co-efficient by definition:

$$X = \frac{O_2'}{O_2'''}, \text{ where } O_2' \text{ is the total oxygen corresponding to the}$$

sample, and O_2''' is the oxygen needed for complete combustion. Units in per cent by volume or lbs-molecules. The former value is ob-

tainable directly as: $O_2' = \frac{1}{3.78} N_2$, because the total of the nitro-

gen is still in the sample. The oxygen needed for complete combustion, that is, to convert the fuel entirely to CO_2 and H_2O , is:

$$O_2''' = CO_2 + CO + 3C_2H_4 + \frac{1}{2}H_2 + \frac{1}{2}H_2O.$$

Referring to the deductions relating to the combustion diagram, we find from equation 1: $\frac{1}{2}(H_2O + H_2) = 3x(CO_2 + CO)$

which gives: $O_2''' = (CO_2 + CO)(1 + 3x) + 3C_2H_4$

As $3x \approx \text{app. } 0.5$, and C_2H_4 is small, this expression may further be simplified to: $O_2''' = (CO_2 + CO + 2C_2H_4)(1 + 3x)$. We get

$$\text{finally: } X = \frac{N_2}{3.78 \times 1.476 c} = 0.179 \frac{N_2}{c} \text{ as co-efficient of excess}$$

air. The nitrogen N_2 is obtained by difference, and c stands for: $CO_2 + CO + 2C_2H_4$. This formula is convenient and is based on the knowledge of the complete gas analysis.

Loss in form of free soot has been neglected in this discussion. The amount of soot formed is under ordinary circumstances very small, in fact too small to show up in heat balance. The unsaturated hydrocarbons are assumed to be C_2H_4 .

IV. DISCUSSION OF RESULTS.

It was primarily considered important to test one combination of burner-boiler very completely. The boiler used for this purpose was

a Cast Iron Sectional Boiler, installed in the university laboratory. The burner was of the guntype, employing emulsification of the oil with some air. It was of the so-called "forced or mechanical draft" type, which merely indicates that a blower is used for artificial or mechanical mixing of the burning gas in the combustion chamber.

The intention was to obtain in this manner characteristics of common nature, that is information applicable in a general way to any small boiler using oil as fuel. Little effort was given to the specific study of definite types of burners, mainly because general information was lacking and partly due to the limited time. The boiler was in no case run as a steam-generator, as this method is entirely incapable of yielding any additional information as regards the questions here taken up, and only tends to decrease the accuracy of the tests.—It might be admitted for example that the combustion efficiency is slightly improved by raising the temperature of the furnace walls from about 100° F. to 212° F. This difference is however far beyond the possibility of experimental detection, and thus does not interest us. Should the question come up however regarding eventual influence of the furnace wall temperatures on combustion, production of soot, etc. a better method of procedure would be to exaggerate conditions by using boiler temperatures of say 500° F. or more. (Mercury boiler).

PRODUCTS OF INCOMPLETE COMBUSTION

Table 1A and figures 11 and 12 give the concentrated results of this part of the investigation. The outstanding feature is the fact that the losses due to incomplete combustion are of a considerable magnitude, in cases even exceeding the dry stack loss. It may further be seen that the CO content only constitutes a negligible fraction of the total amount. Even when the CO content is small enough to escape detection on the ordinary Orsat, the total loss due to incomplete combustion is in some cases found to be as large as 6-10%. The hydrogen is as may be seen of considerable greater importance. A hydrogen contents of 0.7 to 1% may be even be regarded as an average occurrence in watercooled furnaces of this size.

The next feature of interest is the considerable quantity of unsaturated hydrocarbons. It will be seen that the average value of these is around 0.3% at equilibrium condition. It was possible to obtain as much as 1% a few seconds after starting a cold furnace, but the amount dropped very quickly down to the equilibrium value, Fig. 12. This item however is of great influence on the heat-balance, because of the high heat value of these hydrocarbons. The unsaturated hydrocarbons were as far as the calculations of heat value, excess air, etc. are concerned, assumed to be ethylene, (C_2H_4) which is the lowest of its series.

Methane could not be found, except when starting or running at actual gas producer condition, and even then in negligible quantities.

For this reason the determination of methane was entirely discarded at an early stage, that is as far as the ordinary tests were concerned.

GENERAL DISCUSSION OF THE COMBUSTION.

An effort will be made here to outline the conditions favoring the particular type of combustion here encountered. The first question is: Why so much hydrogen in the products of combustion? The second question is: How is it possible to obtain quite large amounts of unsaturated hydrocarbons in the products, while the saturated ones are completely burned?

It is obvious that the combustion is very irregular in nature. It is no reason to believe that each droplet of oil passes through identical stages previous to final combustion. Actually the individual droplets are subjected to greatly different physical conditions. If the velocity of the particles is slow, there may be sufficient time for a complete cracking of the oil. If on the other hand the velocity of mixing is high, there is probably no time left for any cracking in the ordinary sense of this word. In this latter case the hydrocarbons burn more directly, probably with aldehyds and alcohols as intermediate stages. The ignition temperature of the heavier hydrocarbon is in general decreasing as the number of atoms is increased, that is, the heavier it is. It is obvious then, that if such a hydrocarbon is suddenly exposed to a high temperature it will ignite and burn with extreme violence. In other words, the molecule is in a *super-energetic state*. The energy must be released violently, the molecule explodes, and we get detonation.

If the molecule is exposed to no such extreme temperature changes the transformation may be considered as taking place in two steps: Viz. cracking and combustion. If the mixing is poor, we should expect a quite complete cracking of the oil to gaseous products and soot, (and some tar). The physical conditions under which this particular cracking takes place is: High temperature and very low pressure. Some idea may be had concerning the gaseous products to be expected in this and corresponding cases by the following table which shows the gaseous products of regular oil cracking at 900°C and 1 atm. pressure. X₁.

Illuminants	13.1%
Methane	46.7%
Hydrogen	38.6%

These percentages can of course not be expected to give a true picture of our case, because oxygen is present and the partial pressures are very low. A partial combustion will also somewhat disturb the equilibrium. The tendency towards these intermediate products will still exist however.

The point of interest is that we can definitely expect illuminants, methane and hydrogen as products of incomplete combustion. It may

X)1 W. F. Rittman and others: Bulletin 114, Department of the Interior. "Manufacture of gasoline etc." page 32.

also be concluded from a study of oil cracking that the relative quantity of hydrogen should increase with the temperature. This conclusion was largely verified by these tests.

The second question of interest is how considerable amounts of unsaturated hydrocarbons can exist in the products, while on the other hand only negligible quantities from the paraffin series are left. This question is apparently satisfactorily explained by J. Tausz in his theory of super-saturation X)2 of hydrocarbons. This theory states that the saturated hydrocarbons become super-saturated at high temperatures. There are *too many hydrogen atoms* in the molecule. These are thrown off violently and tend to cause detonation. On the other hand, hydrocarbons, which are unsaturated at room temperature, become saturated, that is stable, at higher temperatures. Hence their characteristic as an almost neutral gas, and possibly their relative low combustibility in the high temperature region.

The very low percentage of carbon monoxide may also be explained from a theoretical viewpoint. A study of the equilibrium equation for the water gas reaction furnishes some useful information on this point.

The existing experimental material in this field, regarding the combustion of hydrocarbons consists largely of tests on the lowest members of the different hydrocarbon series. These tests have shown that CO and H₂ are parallel products of combustion. This means that the hydrocarbons at partial air deficiency burn practically completely to CO and H₂. If more oxygen is furnished, the conversion to CO₂ and H₂O will start. This combustion is not "selective" in any respect, but is entirely guided by equilibrium relations. To burn the hydrocarbon to CO₂ and H₂, is for instance, not possible, because the reaction $\text{CO}_2 + \text{H}_2 > \text{CO} + \text{H}_2\text{O}$ immediately would prevent it. On the other hand there is no reason to expect CO and H₂O as final products of incomplete combustion, because of the reverse reaction: $\text{CO} + \text{H}_2\text{O} > \text{CO}_2 + \text{H}_2$ (In a coal fired furnace where the partial pressure of the water-vapor is comparatively small, there is little tendency for this latter reaction, and we get in fact very nearly CO and H₂O as sole products!).

The combustion is in above respects proceeding according to the equilibrium equation for the water-gas reaction: $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$ which is:

$$4.571 \log_{10} K_p = - \frac{18110}{T} + 4.8584 \log_{10} T - 2.4212 \cdot 10^{-3} T + 0.1905 \times 10^{-6} T^2 - 2.9 \text{ refer to X)3}$$

$$K_p = \frac{P_{\text{co}} \cdot P_{\text{h}_2\text{o}}}{P_{\text{co}_2} \cdot P_{\text{h}_2}}$$

where $K_p = \frac{P_{\text{co}} \cdot P_{\text{h}_2\text{o}}}{P_{\text{co}_2} \cdot P_{\text{h}_2}}$ and the P's refer to the partial pressures of the constituents, and $T = ^\circ\text{F absolute}$.

X)2 Dr. J. Tausz: "Zündungsvorgänge in Breenkraftmaschinen" in Jahrbuch der Breenkrafttechnischen Gesellschaft E. V. Funfter Band 1924

X)3 See: University of Illinois Bulletin No. 139, p. 128.

Worked out for 4 different cases we get

at 1000°F.	:	Kp = 0.25
" 1500°F.	:	Kp = 0.90
" 2000°F.	:	Kp = 2.00
" 2500°F.	:	Kp = 3.15

As the ratio $\frac{P_{H_2O}}{P_{H_2}}$ is close to unity for oil fuels, we have conse-

quently: $\frac{P_{CO}}{P_{H_2}} = 0.25, 0.90, 2.00$ and 3.15 respectively for above cases.

At 1000°F. where the combustion may be considered finished*, the ratio of carbon monoxide to hydrogen is 1 to 4. Above figures however only apply to actual equilibrium. The equilibrium between the two components may not be attained for several reasons, but the tendency towards it exists nevertheless. There is thus a probability that hydrogen exists in excess because of the considerable amount formed in cracking at air deficiency.

It is also interesting to note in this connection that the large amounts of hydrogen obtained for several minutes after a "cold" start is exactly what should be expected according to the above analysis. The furnace temperature is in this period very low causing the relative increase in hydrogen. See table 3 and figure 12.

ON DETONATION

It was mentioned before that the ignition temperature of the heavier hydrocarbons is relatively low. In fact the gaseous products seem in general to possess the highest ignition points. It is thus quite inconceivable that the oil always should crack down to gaseous products which are so much the harder to ignite. X)4 If however sufficient time is allowed for a gradual rise in temperature this is apparently what happens, and ordinary slow combustion will take place. If on the other hand the heavy molecules are suddenly exposed to very high temperatures an essentially different kind of combustion will occur. We refer to this type of combustion as detonation. This detonation is the cause of the combustion noise which is typical for some burners. Detonation is identified by a violent increase in pressure, this pressure being under ideal conditions of the magnitude of hundreds of atmospheres. This increase in pressure is the physical criterion of detonation as against ordinary slow combustion. In the latter case no such pressure increase takes place. The detonation velocity is of the order of ten thousand feet per second, while ordinary combustion proceeds at a rate of a few feet only. The saturated hydrocarbons are most likely to be the cause of the detonation, in accordance with the theory of super-saturation previously referred to. The direct reason for this violent kind of combustion is probably that hydrogen is thrown off in large quantities from the heavier molecules. This hydrogen being in

* There is probably a catalytic action of the fire bricks which prevents the "freezing out" of the watergas equilibrium at higher temperatures.

X)4 See: Kruppsche Monatshefte, Jan 1921, page 19.

"status nascendi" is probably acting much in the manner of numerous igniters projecting ahead of the detonation wave. It must be understood that the detonation in a furnace, being of a vague and undeveloped nature, is entirely desirable as far as the combustion is concerned.

INFLUENCE OF OIL-AIR RATIO ON THE COMBUSTION.

By reference to fig. 11 it will be seen that an increase in the amount of excess air does not in general decrease the incomplete combustion loss. This result may not be evident. The explanation is tentatively given as follows:

A large part of the combustion air is, due to imperfect mixing, largely to be considered as secondary air and as such greatly checking the combustion in the outer layer of the flame. The theoretical flame temperature is practically inversely proportional to the air supplied for combustion. A large amount of excess air is then identical with a low average furnace temperature. The combustion time is also cut down in same proportion. Any beneficial effect of the excess air is in other words neutralized by lowering of the furnace temperature and decrease of combustion time.

The detrimental effect of secondary air is shown by comparing the tests 11 and 12, see table 1. These tests were performed on a pot type burner. The loss due to incomplete combustion decreased from 9.7 to 1.8% by tightening up leaks in refractory cement in the base of boiler, which cement was used to seal around burner blast pipe.

The only "excuse" for using any amount of excess air is to avoid production of soot. Excess air "shortens" the flame, thus preventing it from touching the water cooled parts of the furnace. Soot seems to be produced mainly when a cold surface is hit directly by the visible flame. Cold air must probably, to some extent, have the same effect. The actual process of soot production is practically unknown. It appears as if the carbon skeleton of the hydrocarbon in some cases escapes the combustion. This happens presumably in particular with the aromatic hydrocarbons, for example, benzene. The carbon atoms are here held very strongly together while the hydrogen is relatively loose. If once formed the carbon or coke particles are very hard to burn (compare pulverized fuel). The logical solution of the soot problem is then to prevent the formation of soot rather than endeavoring to burn it after it is formed. That is: The visible flame should not touch any water-cooled part, there should be no secondary supply of cold air. (The ultimate achievement in this direction is the "blue" type of flame.)

The serious insulating action of the soot is indicated by test No. 3, where the efficiency obtained was 50.8% while the corresponding value for a clean boiler as interpolated from the efficiency diagram in fig. 10 is 60%. The boiler had a heavy deposit in the gas passages.

STUDY OF STARTING AND INTERMITTENT OPERATION

It was undertaken to study the combustion during the starting period of test 2. The results are shown in table 3 and fig. 12. The loss is quite large during the first two minutes. The analysis at one minute after start of the burner, is for example, as follows:

CO ₂	=	10.00%
O ₂	=	3.82%
C _n h _{2n}	=	0.55%
H ₂	=	2.60%
CO	=	2.72%
CH ₄	=	0.35%

The loss at this moment is not less than 6000 BTU per lb. of oil and is probably close to 35% of the heat value due to some additional soot loss. After 10 minutes the combustion is almost normal except for the hydrogen content, which is persistently very large over a long period. It is to be noted that the final excess air in this test is only 3%, while there is a considerable air deficiency in starting. The test consequently shows eventual tendencies on exaggerated scale. There was a great production of soot, which might be expected.

As a counterpart the starting condition of test 3 was also examined in the same manner, (see table 4). The final excess air is here 90% and there is only a slight extra loss, due entirely to H₂, in starting.

A third study of the starting loss, or more correctly, the chemical part of the starting loss was made of the pot type burner. In this case the flame did not touch any cold parts whatsoever. City gas and some air was added to assist combustion in starting, both furnished automatically. This study was made in connection with test 12. The result is shown in table 5. The chemical starting loss is here negligible.

Test 9 is run intermittently with periods of one half hour on and one half hour off. The average gas sample was collected as usual for the entire test, with exclusion of the "off" periods. The result is shown in the main table 1. The instantaneous efficiency for the test is further shown in fig. 8. These results are very interesting: The loss due to incomplete combustion is no greater than that found in continuous operation and the efficiency is only slightly lower than the value of a corresponding continuous run. The load is 17.75 lbs. of oil per hour, which corresponds to 8.9 lbs. in continuous operation. The continuous efficiency found by interpolation of test data would be about 74% while the efficiency here obtained is 68%. See fig. 10. The difference is practically caused altogether by the cooling effect of the air passing through the boiler when the burner is off.

No tests were run with longer period of shutdown. It is obvious however that if these are extended over several hours, allowing the bricklining to cool down, the chemical loss must be increasing, finally reaching the condition shown in test 2 for a "cold" start.

Tests 1-4 were run so as to include both the starting and the cooling down periods. See figs. 2-5. These tests lasted 4 hours. The equilibrium efficiency is 1-2% in excess of the average efficiency of the whole test. As the fuel-consumption was close to 20 lbs. per hour, a total of 80 lbs. was consumed. One to two per cent consequently represents about 15 to 30 thousand BTU. This heat is consequently lost somewhere. It is not all due to imperfect combustion in starting, but also due to the cooling effect of the air passing through the boiler after shutdown.

Test 12, fig. 7 refers to a pot type burner, with no brick lining in the furnace. In this case, the maximum and the average efficiencies are identical. There is in this case no loss in starting, and the cooling loss is also negligible.

Test 10, fig. 6 is for a gun type burner with a relatively large amount of brick lining in the furnace. The loss is here considerable. Remedy: Shut off air supply when burner is off.

That considerable time is needed in order to bring the furnace up to the final temperature condition is shown in fig. 9, also referring to the same test (10). The cooling is on the other hand quite slow.

INFLUENCE OF OIL USED.

The great majority of the tests were run on 28-32 oil. Tests 8, 8₂, 8₃, 11 and 12 are exceptions, where 38-40 oil was used. No difference whatsoever was found in the general behaviour of the burner. Even the products of incomplete combustion were identical as far as could be ascertained. This result is almost obvious however, as the actual difference in the oils used is too small.

STUDY OF THE HEAT ABSORPTION OF THE BOILER.

It was endeavored to obtain a picture of the heat absorbing qualities of the Cast Iron Sectional boiler when using an oil burner.

Fig. 10 shows the overall efficiency of the clean boiler plotted against the excess air. The continuous increase in efficiency, as the excess air is decreased, is the most surprising feature encountered. The maximum efficiency is virtually to be found at a slight air deficiency. The exact location was not definitely determined however. As pointed out before, the excess air is of no beneficial effect on the combustion and is consequently just increasing the stack loss without compensation elsewhere. If the excess air is greatly increased the efficiency drops down to that of a waste gas boiler, which is the absolute minimum obtainable. This drop is however quite gradual, which fact clearly indicates that the heat transmission due to radiation is of relatively smaller importance as compared with a coal-burning boiler. If thus a certain amount of air, say 300 lbs. per hour, is supplied to the boiler, the efficiency is slowly decreasing as the rate of oil supply is decreased.

Maximum heat absorption is found in the neighborhood of zero per cent excess air and is equal to about 13800 BTU per lb., while the minimum heat absorption at several hundred per cent excess air is in the neighborhood of 10600 BTU per lb. In other words, no severe falling off in efficiency occurs. This appears so much more surprising as this particular boiler was very unfavorable in this respect, due to lack of adequate in-direct heat absorption surface area. The mentioned efficiency drop of 3200 BTU can easily be cut in half by addition of more heat absorbing surface area. The efficiency of the oil burning boiler is not very much dependent upon the excess air, if sufficient indirect heat absorbing surface area is present, and the boiler not overloaded. The entire possible difference for a boiler of satisfactory design is of the order of 10%. The temperature in the middle of the first pass was observed in the majority of the tests. It was possible to calculate the temperature at the outlet of the furnace proper. This temperature is given in table 2. The heat absorbed in the furnace could be calculated, and also the heat absorbed by the indirect area. The maximum heat that possibly can be used by the boiler is the lower heat value of the fuel, less the loss in incomplete combustion. This value corresponds to 100% in fig. 13, radiation being neglected. The interesting result shown in this figure is that only about 10% of the heat is absorbed in the indirect passages of these boilers at ordinary conditions of load and excess air. This latter area might have been several times larger and the cross section of the passages greatly reduced. Ample draft is present for this purpose: The proper load for the boiler is not in excess of 300 lbs. of products per hour, while a load of 700 lbs. could easily be carried by means of a stack equivalent to that of a 2-story dwelling. (Test 7). The boiler is thus at proper operating condition only utilizing approximately $(3/7)^2$ or less than one fifth of the available draft!

V. GENERAL SUMMARY OF RESULTS.

It is found that there usually is a large loss due to incomplete combustion, in magnitude comparable to that of the dry stack loss. The products of incomplete combustion is found to consist largely of hydrogen and unsaturated hydrocarbons, while only negligible amounts of carbon monoxide and methane is present. It is found that the heat value lost due to soot production is negligible, while the indirect loss caused by clogging of the flues is of a more serious nature.

The important question of intermittent operation was subjected to an extensive study of its various aspects. It may be stated as an axiom that if the periods of shutdown are short, and no air is allowed to pass the boiler during this period, there is no loss except in form of increased radiation from the boiler surface to the surroundings. If, also, the insulation of the apparatus is perfect, the loss caused by intermittent operation is necessarily zero. Any loss due to intermittent operation is due to deviations from above conditions. For a furnace containing no brick lining, the condition imposed as regards the periods of shut-

down may be dropped. It is found that the loss in this case, even from a "cold start", that is for an infinite period of shutdown can hardly be detected. This type of furnace is consequently by far the most flexible, and beyond question the most desirable where comparatively extended periods of shutdown are to be expected.

This type of furnace can of course only be used for certain types of burners, while in other cases a brick lining is necessary in order to promote proper combustion. Referring to this latter case, it was found that there is a definite measurable loss due to aggravated incompleteness in the combustion whenever the burner is turned on and the flame hits the cold bricks. The fact is obvious, although no material could be found in the literature referring to actual measurements of such losses.

The most exaggerated case of a "cold start" with the burner adjusted for almost no excess air, has been most carefully examined. The total chemical loss at one minute after start is, for example, found to be in excess of one-third of the heat value. It is shown on the other hand that for regular intermittent operation, with periods of shutdown of one-half hour, no measurable loss comes from this source.

By far the largest part of the loss is, however, caused by the air being sucked through the furnace and boiler after shutdown. This effect is detrimental for two reasons: directly, because otherwise useful heat is unnecessarily carried up the stack, and indirectly, because the temperature of the brick lining is unnecessarily lowered. It is mainly on this point that the type of burner employing some kind of continuous operation is superior.

It will be useful to refer to these stack losses as consisting of two kinds, viz., the customary loss, and the loss after shutdown. It should be entirely possible to avoid this latter loss by using tight boilers and positively shutting off the air supply through burners or other openings. Even an opening of one-quarter of a square inch should not be permissible.

Regarding the loss due to radiation at intermittent operation, this question is not so important, because some radiation loss may even be quite desirable, as far as domestic boilers are concerned. This loss may, however, also be divided in two parts; the ordinary radiation loss, and a loss due to radiation after the burner is shut off. If the boiler is being used as a high temperature steam generator, these losses will gain in importance, both representing appreciable items in the heat balance.

Regarding the question of boiler efficiencies, it is hoped that the results embodied in the curves of Figure 10 will be of value. It must be pointed out that the efficiency is largely independent of the burner, provided it is of a reasonable design. That is, the efficiency depends mainly on the heat absorbing qualities of the boiler proper, although it must be pointed out that certain combinations of boiler-burner are more favorable than others. The most important fact pointed out as regards the boiler efficiency is that its maximum is to be found at or at least very near the theoretical oil-air ratio.

TABLE 1: BOILER TESTS,
GENERAL DATA.

Test No.	Burner Used	Boiler Used	Oil Used	Load Lbs. of oil per hour	Coefficient of excess air	Total air per hour, lbs.	Total products per hour, lbs.	Temperatures of Stack	Room
1	A	S-7	28-32°	19.50	1.48	414	433	750	78
2	"	"	"	19.12	1.03	282	301	740	82
3	"	"	"	19.12	1.90	521	540	850	82
4	"	"	"	19.37	1.28	357	376	805	88
5-1	"	"	"	20.87	1.51	452	473	720	76
5-2	"	"	"	19.37	2.12	590	609	750	76
5-3	"	"	"	19.50	1.07	299	318	630	76
5-4	"	"	"	19.50	1.25	350	369	680	77
6-1	"	"	"	19.75	1.99	563	583	765	84
6-2	"	"	"	31.62	1.25	568	600	930	86
7-1	"	"	"	32.50	1.43	668	700	890	88
7-2	"	"	"	13.52	2.80	548	562	625	89
7-3	"	"	"	12.87	1.41	261	274	565	89
8-1	"	"	38-40	21.75	2.02	632	654	780	82
8-2	"	"	"	21.25	1.47	448	459	750	76
8-3	"	"	"	20.75	1.14	340	361	700	81
9	"	"	28-32	17.75	1.25	319	337	670	82
10	"	"	"	18.37	1.31	346	364	560	75
11	B	"	38-40	13.50	1.10	213	226	550	76
12	B	"	"	13.50	1.10	213	225	550	74
13	A	S-6	28-32	13.25	1.31	247	260	520	75
14	"	"	"	10.50	0.88	133	143	460	75

TABLE 1-A BOILER TESTS
GENERAL DATA.

Test No.	GAS ANALYSIS				
	CO ₂	O ₂	III	H ₂	CO
1	9.2	8.2	0.1	0.8	0.4
2	12.9	3.4	0.4	0.5	0.4
3	6.9	11.3	0.35	0.4	0.5
4	10.6	6.3	0.35	0.65	0.1
5-1	9.4	7.7			
5-2	6.9	11.3			
5-3	13.8	2.0	0.0	0.55	0.1
5-4	11.9	4.5			
6-1	6.6	10.8	0.15	0.5	0.15
6-2	11.4	5.2	0.17	0.9	0.0
7-1	10.0	7.10	0.12	0.5	0.0
7-2	4.7	14.3	0.22	0.0	0.0
7-3	10.0	7.1	0.17	0.65	0.0
8-1	7.1	11.1	0.0	0.33	0.1
8-2	9.1	6.6	0.25	0.75	0.0
8-3	12.2	4.1	0.32	0.60	0.1
9	10.9	5.8	0.36	0.70	0.1
10	11.0	5.8	0.0	1.0	0.15
11	12.1	3.6	0.25	1.5	0.7
12	13.6	2.1	0.0	0.65	0.0
13	10.2	6.4	0.3	1.10	0.4
14	13.6	2.4	0.5	1.0	1.7

Run with heavy soot deposit in flues.

No complete analysis.

Intermittent operation.

Air deficiency.

TABLE 1-B: BOILER TESTS
GENERAL DATA.

Heat Balance B T U per lb. of Oil								
Test No.	Heat value of oil	Useful Heat	Dry Stack Loss	H ₂ O		Incomplete Combustion	Radiation (app.)	Error
				Loss				
1	19300	11800	3590	1620		1345	750	-195
2	"	13000	2480	1630		1840	800	450
3	"	9800	5340	1640		2240	700	420
4	"	12200	3330	1645		1770	750	395
5-1	"	12700	3250	1645		1400	700	395
5-2	"	11500	4600	1640		1200	700	340
5-3	"	13900	2150	1580		360	800	-510
5-4	"	13600	2500	1620		1100	750	270
6-1	"	11000	4900	1610		1440	700	350
6-2	"	11800	3880	1700		1150	700	-70
7-1	"	11800	4170	1690		900	700	-40
7-2	"	10600	5230	1540		1700	700	470
7-3	"	13200	2410	1540		1240	800	-110
8-1	19700	11100	5190	1640		415	700	-655
8-2	"	12200	3680	1610		1570	700	60
8-3	"	13300	2570	1650		1400	750	-30
9	19300	13100	2670	1560		1790	750	570
10	"	13500	2290	1540		770	1000	-200
11	19700	13800	1890	1485		1910	500	-115
12	"	14700	1870	1510		350	500	-770
13	19300	13250	2100	1485		2100	800	435
14	"	13800	1220	1435		2500	800	455

TABLE 1-C: BOILER TESTS
GENERAL DATA.

Test No.	HEAT BALANCE PERCENT				
	Useful Heat	Dry Stack Loss	H ₂ O Loss	Incomplete Combustion	
1	61.2	18.6	8.4	7.0	4.8
2	67.3	12.9	8.5	9.5	1.8
3	50.8	27.7	8.5	11.6	1.4
4	63.2	17.3	8.5	9.2	1.8
5-1	65.8	16.8	8.5	7.2	1.7
5-2	59.6	23.8	8.5	6.2	1.9
5-3	72.0	11.2	8.2	1.9	6.7
5-4	70.4	13.0	8.4	5.7	2.5
6-1	57.0	25.4	8.3	7.4	1.9
6-2	61.2	20.1	8.8	6.0	3.9
7-1	61.2	21.6	8.8	4.7	3.7
7-2	54.9	27.1	8.0	8.8	1.2
7-3	68.4	12.4	8.0	6.4	4.8
8-1	56.5	26.3	8.3	2.1	7.0
8-2	62.0	18.7	8.2	8.0	3.1
8-3	67.5	13.0	8.4	7.1	4.0
9	68.0	13.8	8.1	9.3	0.8
10	70.0	11.9	8.0	4.0	6.1
11	70.0	9.6	7.5	9.7	3.2
12	74.6	9.4	7.7	1.8	6.5
13	68.6	10.9	7.7	10.9	1.9
14	71.4	6.3	7.4	12.9	2.0

Run with heavy soot deposit in flues.

No complete analysis, data estimated where necessary.

Intermittent operation.

TABLE 2: DATA ON HEAT ABSORPTION
Sectional Boiler S-7

Test	Temperatures of		Total	BTU per lb of oil		Absorbed in Furnace
	Stack	Leaving Furnace		Lost in Stack	Absorbed in flues	
5-1	720	1140	15950	3250	2400	10300
5-2	750	1100	16100	4600	2700	8800
5-3	630	1010	16050	2150	1500	12400
5-4	680	1090	16100	2500	1900	11700
6-1	765	1110	15900	4900	2600	8400
6-2	930	1355	15680	3880	2000	9800
7-1	890	1360	15970	4170	2500	9300
7-2	625	900	15830	5230	2800	7800
7-3	565	900	15610	2410	1750	11450
8-1	780	1080	16290	5190	2200	8900
8-2	750	1070	15880	3680	1750	10450
8-3	700	1080	15870	2570	1600	11700
9	670	920	15770	2670	1150	11950
11	550	955	15690	1890	1650	12150
12	550	905	16570	1400	1850	13320

TABLE 2-A: DATA ON HEAT ABSORPTION
Sectional Boiler S-7

Test	Total	Lost Stack	Absorbed in Flues	Absorbed in Furnace
5-1	100	20.3	15.2	64.5
5-2	100	28.7	16.8	54.5
5-3	100	13.4	9.3	77.3
5-4	100	15.6	11.8	72.6
6-1	100	30.7	16.3	53.0
6-2	100	24.7	12.7	62.6
7-1	100	26.1	15.6	58.3
7-2	100	33.0	17.6	49.4
7-3	100	15.4	11.2	73.4
8-1	100	31.8	13.5	54.7
8-2	100	23.2	11.0	65.8
8-3	100	16.2	10.1	73.7
9	100	16.9	7.3	75.8
11	100	12.0	10.5	77.5
12	100	8.5	11.2	80.3

TABLE 3: STARTING CONDITIONS,
Complete Gas Analysis Obtained in Connection with Test 2.

Time After Start	CO ₂	O ₂	H ₂	CO	Illuminants Cnh2n	Paraffines Cnh2n+2
1 min.	10	3.28	2.60	2.72	0.55	0.35
1.5 min.	12.3	1.23	2.05	3.0	0.75	0.30
2 min.	12.9	1.95	2.73	0.26	0.59	0
5 min.	13.5	1.59	1.53	0.25	0.57	0
10 min.	10.3	2.85	1.39	0.13	0.32	0
Final	12.9	3.4	0.5	0.4	0.4	0

(from an earlier test)

TABLE 4: STARTING CONDITION
Test No. 3, Gas Analysis.

Time After Start	CO ₂	O ₂	H ₂	CO	Illuminants Cnh2n	Paraffines Cnh2n+2
1 min	7.2	10.1	0.9	0.05	0.4	0
2 min.	7.1	10.5	0.7	0.05	0.4	0
Final	6.9	11.3	0.40	0.05	0.35	0

Cnh2n Cnh2n+2

TABLE 5: STARTING CONDITION
Obtained in Connection With Test 12 on Pot Type Burners.

Time	CO ₂	O ₂	H ₂	CO	Illuminants Cnh2n	Paraffines Cnh2n+2
5 min.	13.4	2.82	0.20	0.0	0.13	0.0
10 min.	13.1	3.25	0.12	0.0	0.05	0.0
Final	13.6	2.1	0.65	0.0	0.0	0.0

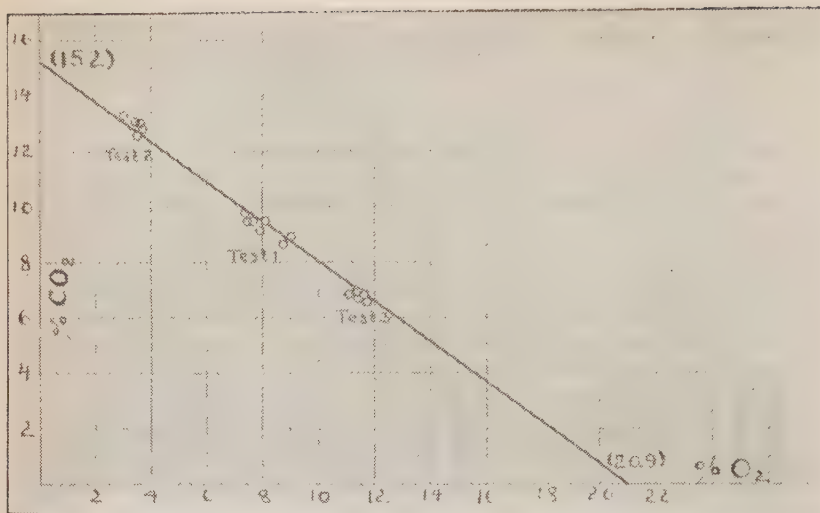
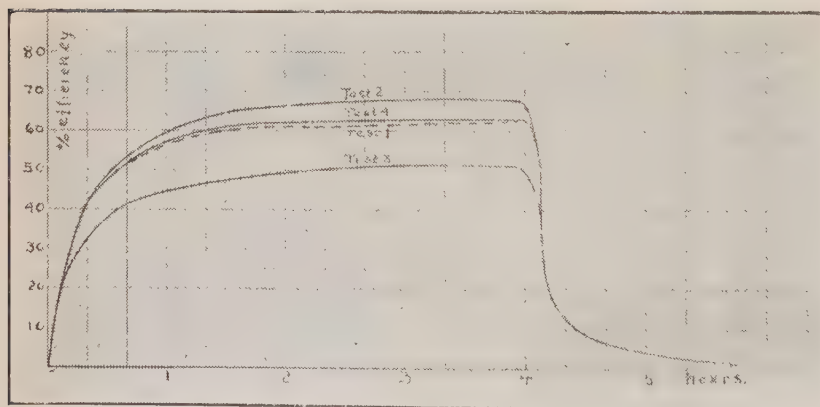


Fig. 1. Ostwald combustion diagram. Points are plotted from tests no. 1-4.



Figs. 2-5. Showing instantaneous efficiencies of tests 1-4. American Radiator S2307. Gun-type burner. Load app. 20 lbs. per hour. Note that starting and cooling are included.

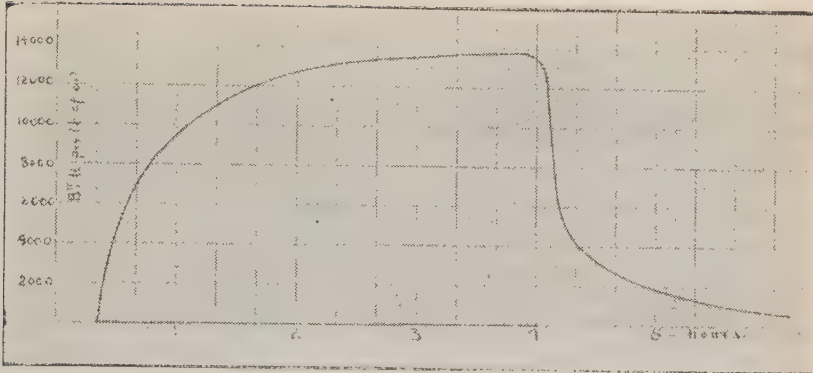


Fig. 6. Showing instantaneous output of test 10 in BTU per lb. of oil. American Radiator S2307. Gun-type burner. Heavy brick-lining. Note slow starting and cooling down.

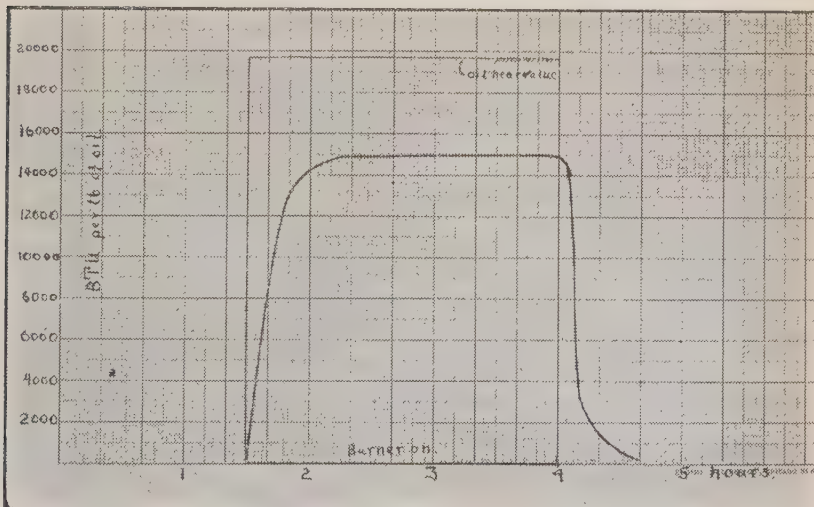


Fig. 7. Showing instantaneous efficiencies of test 12 in BTU per lb. of oil. American Radiator boiler S2307. Pot-type burner. No bricks in furnace. Note rapid starting and cooling down.

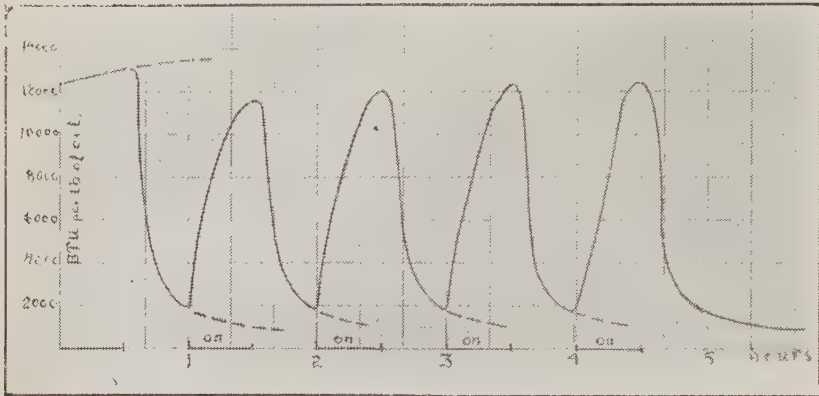


Fig. 8. Intermittent operation. Period $\frac{1}{2}$ hr.— $\frac{1}{2}$ hr. Test 9. American Radiator S2307. Gun-type burner.

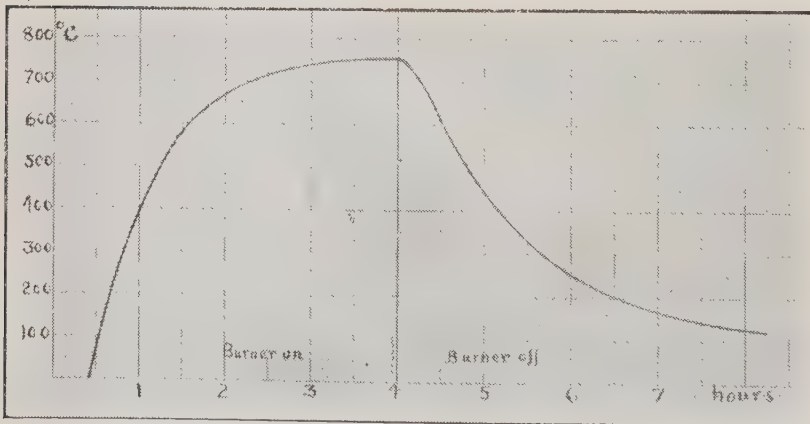


Fig. 9. Representative furnace temperature from test 10. American Radiator S2307. Gun-type burner. Thermocouple located app. in center of furnace, protected by firebricks. Note slow changes.

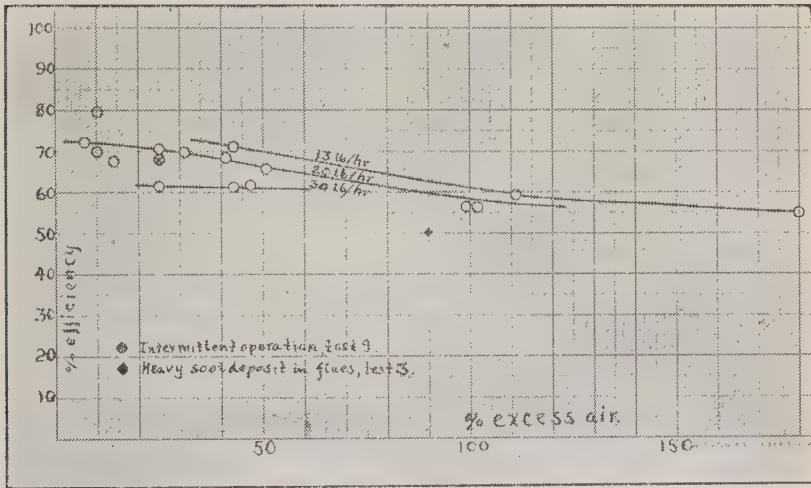


Fig. 10. Complete efficiency diagram. Obtained on American Radiator S2307. Efficiencies vs. excess air.

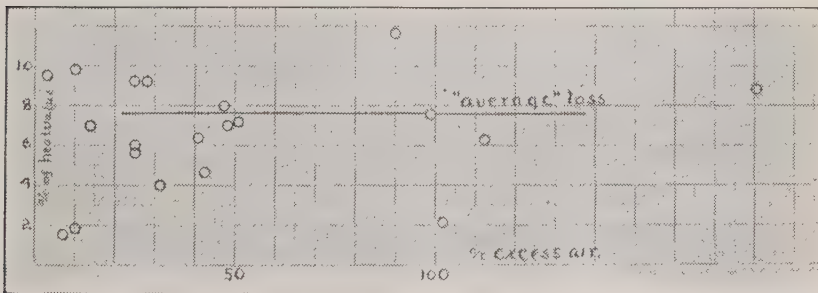


Fig. 11. Losses due to incomplete combustion vs. excess air. No decrease in loss with increase in air.

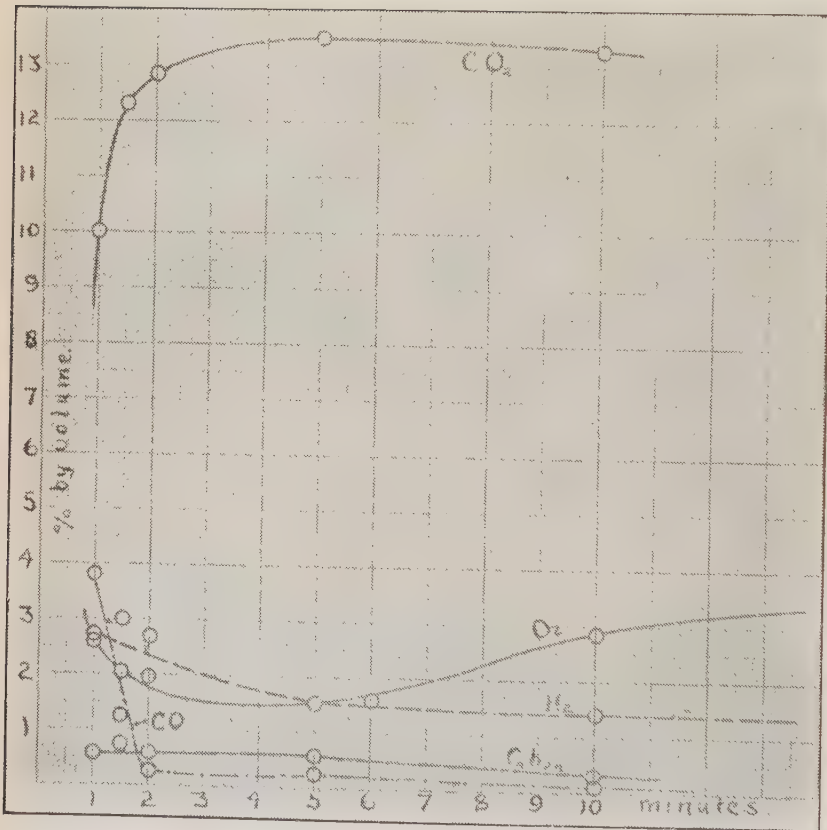


Fig. 12. Products of incomplete combustion plotted vs. time after start in minutes. Obtained on American Radiator S2307 with gun-type burner. Test 2. Final excess air 3%.

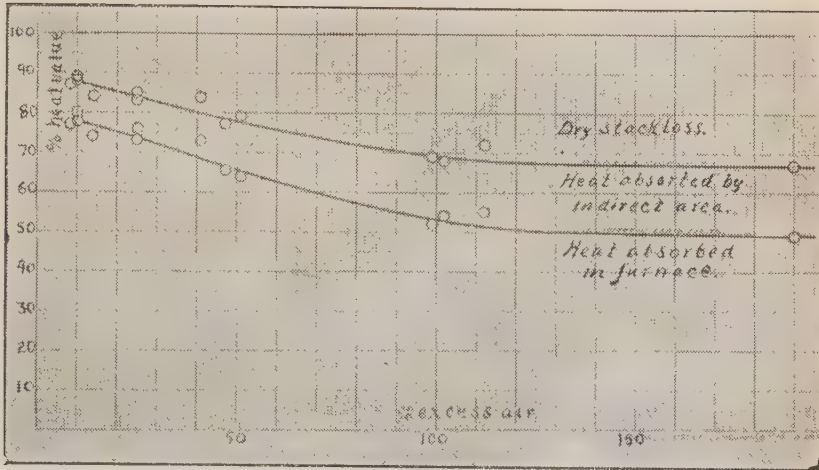


Fig. 13. Diagram showing the heatabsorbption of boiler based on the heat actually liberated in combustion. American Radiator S2307. Note low heatabsorbption in flues.

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BIOGRAPHY

Theodore Theodorsen, son of Ole C. Theodorsen and Andrea, nee Larsen, was born in Sandeherred, Norway on January 8, 1897. His early education was received in the Public Schools of Sandeherred and the Middle School of Sandefjord. He received his "examen artium" from the Larvik Gymnasium and entered The Norwegian Institute of Technology at Trondhjem, Norway in 1917. He received the degree of Dipl. Ing. in Mechanical Engineering in 1922 and was simultaneously, in recognition for scholastic achievements, appointed Research Fellow in Mechanical Engineering at this Institution. He conducted during this time, under the direction of Professor A. Watzinger, researches on heat transfer, vibration of compressor valves, and various other problems. From 1923 he occupied a position as instructor in Mechanical Engineering at the same Institution. He entered the United States on August 25 of the following year, taking up his residence in Baltimore, Maryland. He was then appointed Instructor in Mechanical Engineering at the Johns Hopkins University, a position he has occupied until the present time 1929, teaching classes in engineering mechanics, and thermodynamics. In addition to various engineering jobs, he completed during this time an extensive research on the combustion of oil in small furnaces which study is presented as a part of this dissertation. In 1928 he registered as a student in the Graduate Department of Physics. During 1928-29 he has pursued courses in Physics under Professor K. F. Herzfeld, Professor A. H. Pfund, Professor J. C. Hubbard, Professor R. W. Wood, and in Mathematics under Professor F. D. Murnaghan.

